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# Horizon Free Radical Camera Speed Film

MARCH 1974

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☐ MICROFILMED

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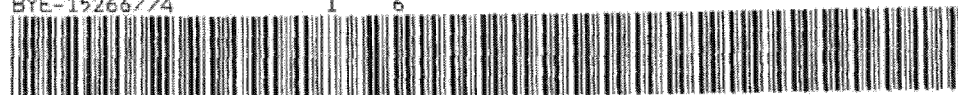
HORIZONS FREE RADICAL CAMERA

SPEED FILM

BYE-15266/74

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MARCH 1974

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PREFACE

This report presents a summary of the Free Radical Film Development Program being carried out at Horizons Research Incorporated, Cleveland, Ohio. The Free Radical System is a very high resolution molecular dye medium capable of producing camera speed film. This project has been sponsored under the auspices of the National Reconnaissance Office (NRO) and managed by the Central Intelligence Agency (CIA). This report discusses the background of Free Radical Film development and the rationale for its use in National Reconnaissance Program (NRP) Systems. In addition, the theory of Free Radical reactions, current status, and the future program plan are presented.

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SECTION I

BACKGROUND

1.1 INTRODUCTION

Current photographic reconnaissance systems in the National Reconnaissance Program (NRP) are extremely limited by the choice of films which can be flown. The most commonly used film in the NRP today is Film Type 1414 which is on a 1.5 mil Estar base. This film type has an aerial film speed of 15.0 and a low contrast (1.7 : 1) resolving power of 260 cycles/mm.

Even though 1414 is the highest resolution film currently used, it is rapidly becoming a significant limiting factor to ultimate system performance. In other words, the state-of-the-art of today's satellite reconnaissance systems has achieved a level of performance where the recording medium is a contributor to performance degradation. An example of this is shown in Figure 1-1, where the nominal MTF of the HEXAGON Optical System is compared with the MTF of 1414. It can be seen that the MTF of the film is nearly identical to that of the lens, a situation which results in recording less information than the lens is basically capable of transmitting. The final reduced MTF is shown as Curve C.

Table 1-1 shows a comparison of Free Radical versus Film Type 1414. It can be seen from these values that if Free Radical were flown in the HEXAGON System that performance would improve by approximately 40 percent.

TABLE 1-1  
COMPARISON OF FREE RADICAL VERSUS 1414 PERFORMANCE WITH  
HEXAGON AT 82 NM ALTITUDE

Solar Altitude (degrees)	Ground Resolved Distance (GRD)	
	Free Radical (feet)	1414 (feet)
10	2.0	2.9
30	1.8	2.4
50	1.5	2.2

NOTE: These are two sigma low values.

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# COMPARISON OF HEXAGON LENS (MTF) AND 1414 FILM TYPE (MTF)

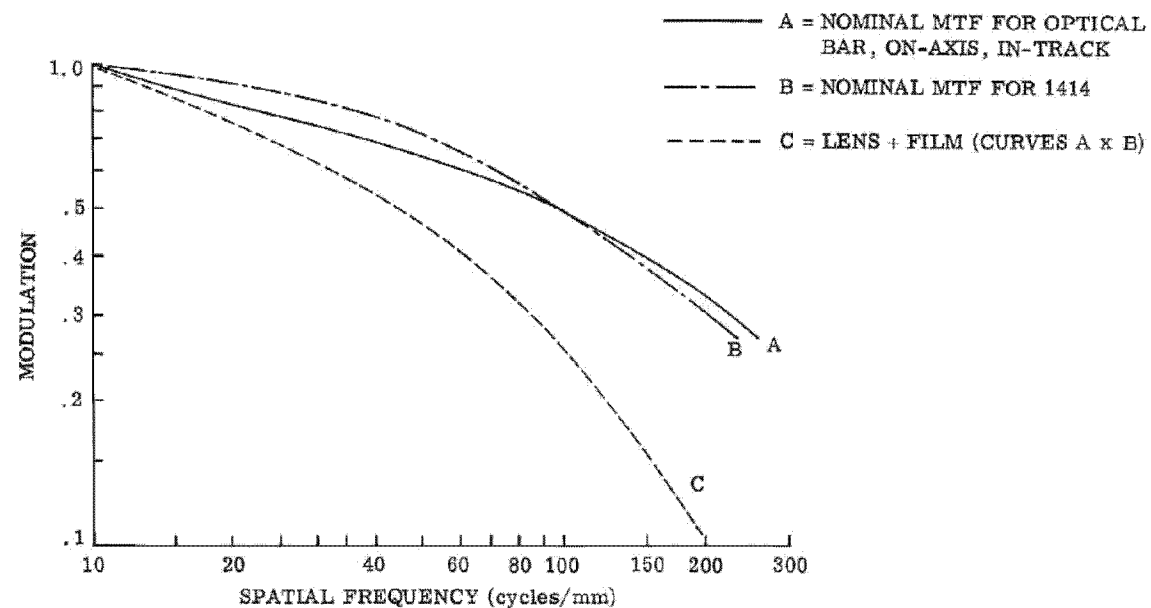


FIGURE 1-1

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It is our goal to attain a recording media that maximizes system capability and, hence, minimizes informational loss. The fundamental problem, however, is the inherent limitation of the silver halide recording media.

Because of the fundamental nature of silver halide recording materials, there is always a speed/resolution trade-off. Figure 1-2 illustrates this point. This figure plots speed versus resolving power for several of the more common aerial films. It can be seen that there is a log-linear relationship between speed and resolving power. What this means is, that if major improvements in film image quality are to be made, they will only be achieved with significant losses in speed. The conclusion is that significant improvements in image quality of silver halide films are not practical while maintaining usable camera speed.

The problem can be summarized as follows:

- A. Current silver halide films are causing a reduction in the optimum performance of the satellite systems.
- B. To maximize performance of NRP photo/optical systems, higher resolution films are necessary.
- C. Significant practical improvements in the image quality of silver halide films is not expected based on the current emulsion technology.

## 1.2 HISTORICAL SUMMARY

The term "Free Radical Photography" was coined at Horizons Incorporated to identify a new light-activated color-forming chemical reaction invented by Dr. Eugene Wainer in 1958. The name originated from the belief that the color-forming reaction was initiated by the splitting of carbon tetrabromide under the influence of light into two free radicals ( $\text{Br}\cdot$  and  $\text{CBr}_3\cdot$ ) which was then followed by chain-propagated condensation or oxidation reactions yielding several molecules of dye for each photon absorbed. This reaction and the mechanism of formation of the dye was first disclosed at the Rapid Processing Symposium held in Washington, DC, on October 15, 1960. This and other photo-chemical reactions were covered under United States Patent No. 3,042,515 (July 1962). Since this time, approximately 100 patents have been issued and/or applied for.

Sample coatings and a briefing of these light-sensitive materials were given to representatives of the Air Force. This led to a contract being awarded on December 1, 1959. The goal of this contract was further improvement of the process and included: (1) extending the spectral sensitivity into the visible region, (2) increasing photo-speed, and (3) investigating the chemistry of the process. The first year's work resulted in discovery of a new visible light-sensitive system based on mixtures of styryl or cyanine dye bases activated by carbon tetrabromide.

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# NOMINAL SPEED VERSUS NOMINAL LOW CONTRAST RESOLVING POWER FOR SEVERAL AERIAL FILMS

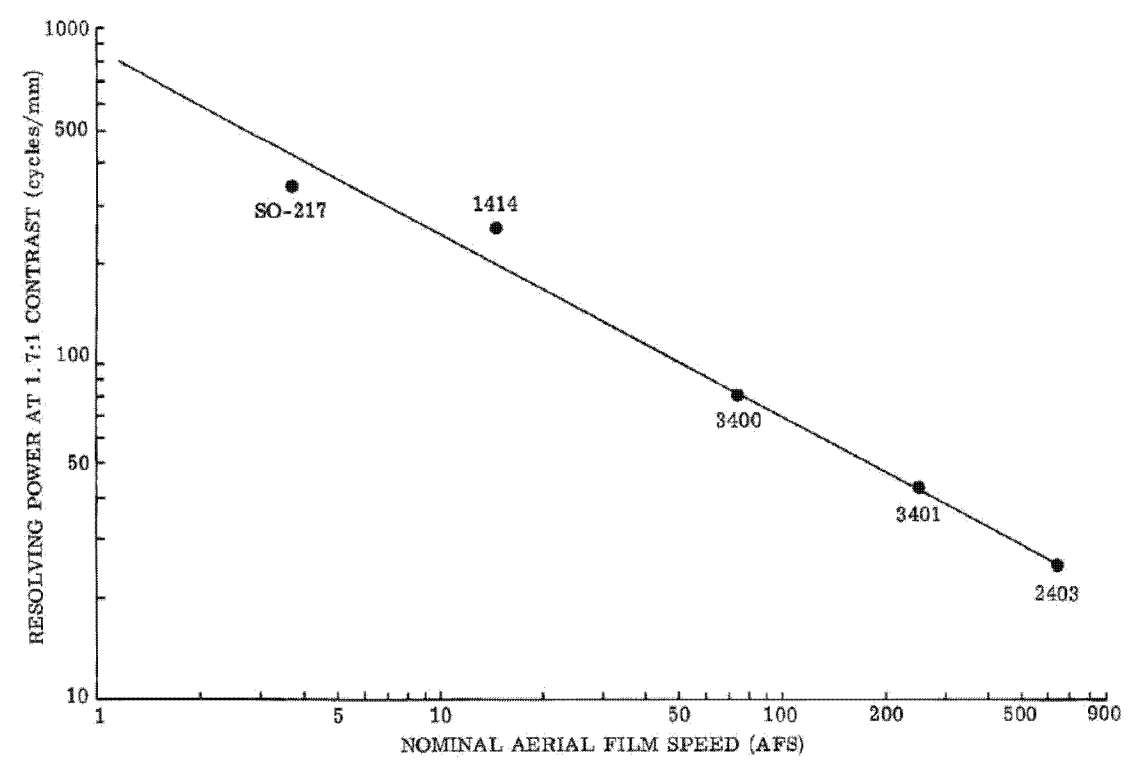


FIGURE 1-2

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As a result of the first year's work, the Air Force awarded a follow-on contract starting in February 1961. During the second year's work, three different photo-systems were investigated. Work on all three photo-systems was undertaken in the following areas: (1) analysis of image dyes, (2) study of reaction mechanisms, (3) improvements in speed and spectral response, (4) synthesis and testing of new activator compounds, (5) speed increases through variation of formulation, (6) investigation of dry-fixing methods, and (7) studies on the quantum yield of the photo-reaction. Considerable progress was made in all phases of the work. Good quality hand coated films of the carbocyanine base system were made on a Mylar base which had jet black image color, excellent continuous tone, medium contrast gradation, and a resolution of at least 250 lines per millimeter. Solvent fixing was still required, and speed was relatively low.

Support for this work was continued by the Air Force starting in February 1962. The research was directed along the same lines as the prior year's contract except for a new emphasis on fundamental studies of the kinetics of the free radical image forming reactions. A survey was made of all literature dealing with free radical and autoxidation reaction mechanisms, with particular reference to inhibitors and accelerators of chain reactions and kinetic studies of these phenomena.

Government sponsorship continued along the same research lines through the end of 1966. The main thrust of this effort was directed at formulation development. Film speed continued to increase. By the middle of 1965, the speed was approaching an ASA of 0.01 or roughly a 1,000 times speed increase over the initial process. There is no direct correlation between ASA and AFS speeds; generally however, ASA speeds are 2 to 3 times greater than AFS speeds.

Also, in mid-1965, it was found that a uniform post-exposure to selected radiation of longer wavelength than the image exposing radiation produced image amplification on the order of 100 to 10,000 times. This dry development process has been termed Red-Lite Development (RLD) and was a main impetus for proceeding on to a camera speed film. In the same time period, a limited effort was sponsored by the Air Force on a higher speed leuco system.

In the period from 1967 thru mid-1969, the emphasis on Free Radical Systems shifted to Duplicating and Laser Recording films.

By January 1969, the following Free Radical Systems had been developed:

A. Aromatic Amine Condensation System

A low speed printout system with no RLD processing capability.

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B. N-vinyl Carbozole System

A low speed photo-polymerization system best employed for photo-resist applications.

C. Dye Base System

A system comprising an aromatic amine dye base and an acid to produce a color dye with RLD capability.

D. Leuco Systems

Good speed systems capable of RLD processing.

The latter two systems are the ones which form the basis of the current system.

In the latter part of 1969, new emphasis was placed on the development of camera speed films. The shelf life problem and spectral sensitization were of prime concern. By the end of 1970, ASA speeds of 5 to 10 had been demonstrated and spectral sensitivity to 610 nanometers had been produced. The shelf life was still poor (15 to 30 minutes), and the gamma and contrast were low.

During 1971, poly-vinyl alcohol (PVA) overcoats were investigated to increase shelf life. By mid-1972, an overcoat was found that significantly improved the film's shelf life.

In late 1972, a new binder material was utilized and better chemical inhibitors were discovered leading to improved photographic properties.

During 1973, the emphasis was concentrated on developing a chemistry that would lend itself to machine coating.

Figure 1-3 presents a technical summary of the development and significant milestones of the Free Radical Film Development Program.

1.3 SUMMARY OF FREE RADICAL ADVANTAGES

The following is a summary of some of the advantages of using Free Radical versus the silver halide films:

- A. Higher resolution which is possible due to the molecular structure of the dye image versus the larger grain size in silver films.
- B. No grain noise versus large level grain noise in silver. This feature allows for a higher DQE on the order of 30% to 40% versus 1% to 2% for silver halide. This indicates that Free Radical is more capable than the silver films of recording low contrast, low detectability images.
- C. Since they are grainless, Horizons' camera speed films show much greater potential for computer dissection, reconstruction, and manipulation than anything possible with silver grain materials.
- D. The image in Horizons' camera-speed films appears to be one which is formed throughout the entire depth of the photo-sensitive

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GOVERNMENT CONTRACT SUPPORT AND MAJOR TECHNICAL MILESTONES

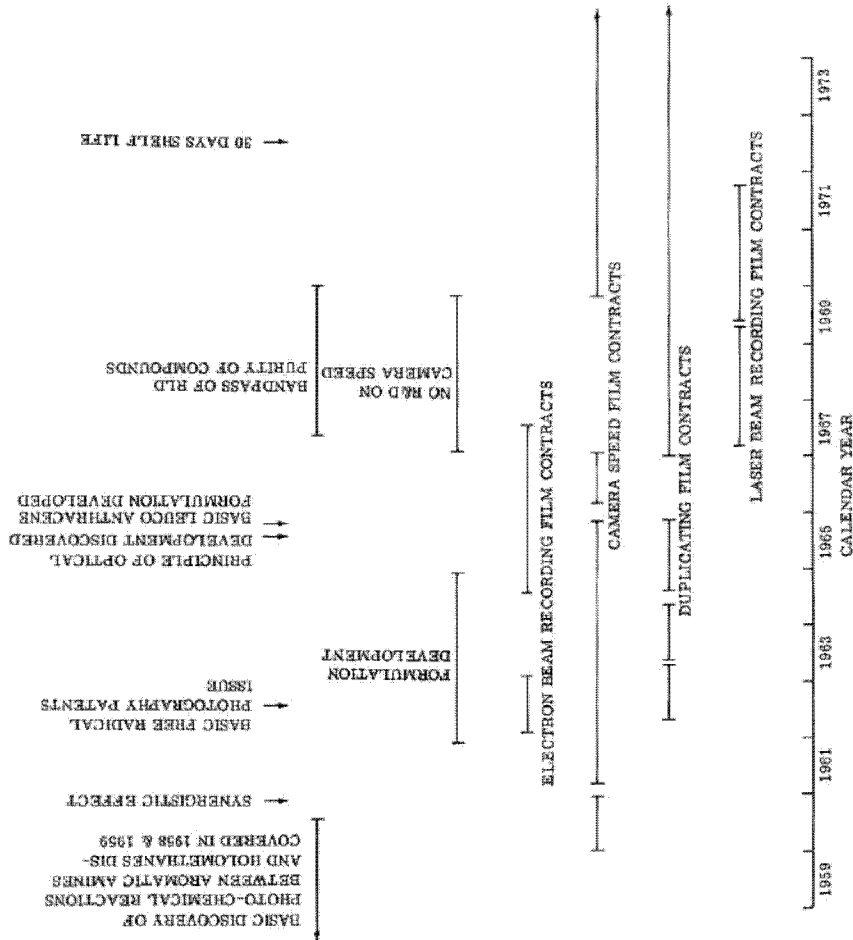


FIGURE 1-3

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layer. Experimental evidence indicates that the image is not a surface, middle, or lower layer image. This implies a wider range of focus than silver films allow when these materials are used in the camera. The critical focus problem experienced with most high resolution camera systems utilizing silver halide film could be relieved by the use of this material.

E. The dye image is an absorbing and not scattering material; therefore, subsequent duplications of this high resolution dye image would also produce images of finer detail and higher resolution.

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## SECTION II

### THEORY

#### 2.1 INTRODUCTION

Free Radical photography may be defined chemically as the formation of dye as a consequence of exposure to electromagnetic or corpuscular radiation of a composition containing a dye intermediate and a Free Radical progenitor. In some cases, the dye intermediate itself may be the Free Radical progenitor.

#### 2.2 DESCRIPTION OF FILM AND PROCESS

Horizons' Camera Speed Film depends on the formation of organic dye molecules (visible dye) as a useful image, see Figure 2-1 for a diagram of the chemistry involved in the dye-forming reactions. The useful image is produced from the formation of a light-sensitive complex between an organic halide compound called the "activator" and the dye former which is an organic amine. The dye former in the Horizons' Camera Speed Film is referred to as D-260. The photographic layer of the film is composed primarily of the dye former and the activator in a mixture which also includes a plastic binder. When exposed to light, the absorption of a photon leads to the breaking down of the complex and the production of an energetic one electron species called "free radicals". The reaction proceeds to the point where the end is the formation of a stable organic dye molecule.

The processing after exposure closely parallels the steps which are found in silver halide film processing. After exposure, the latent image is amplified by the Red-Lite Development (RLD) Process. This optical development process is portrayed in Figures 2-2 thru 2-4. This is the counterpart of liquid development in silver halide photography. During this process, the film is exposed to a uniform selective wavelength red light exposure which is currently within the range of 665 to 725 nanometers. The choice of the development wavelength is tied to the amplification desired and the particular combination of ingredients in the photo-sensitive layer. This development process is capable of amplifications in the order of 1,000 to 100,000 times. It appears that the RLD Process works by the image dye absorbing light at a longer wavelength than the photo-sensitive complex. The photo-sensitive complex was previously given as being composed of the dye former and the activator. The Red-Lite Development Process is selective, as is the silver film organic development cycle. Only the latent image dye absorbs the longer RLD

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# CHEMISTRY OF DYE-FORMING REACTIONS

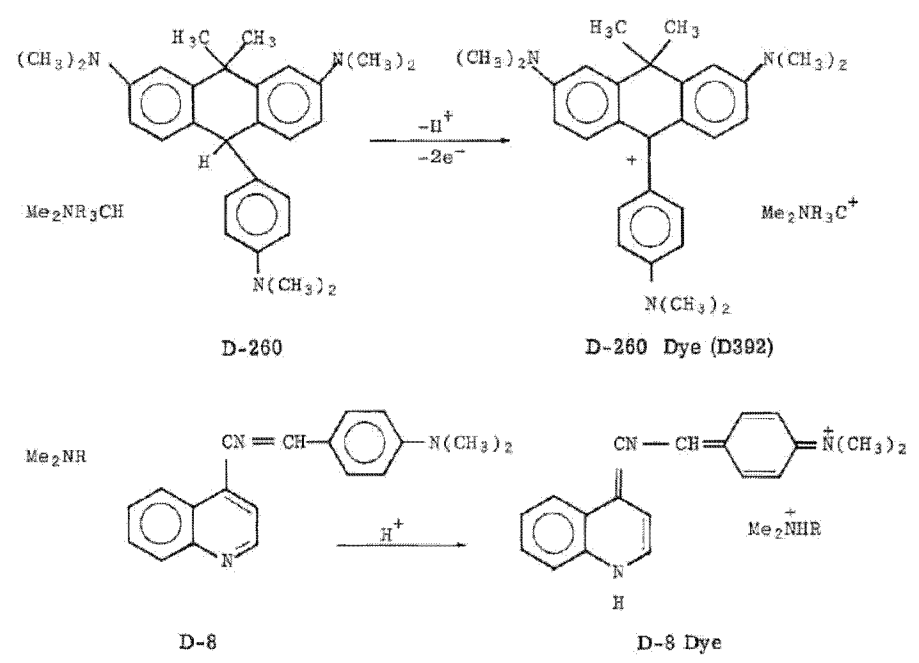


FIGURE 2-1

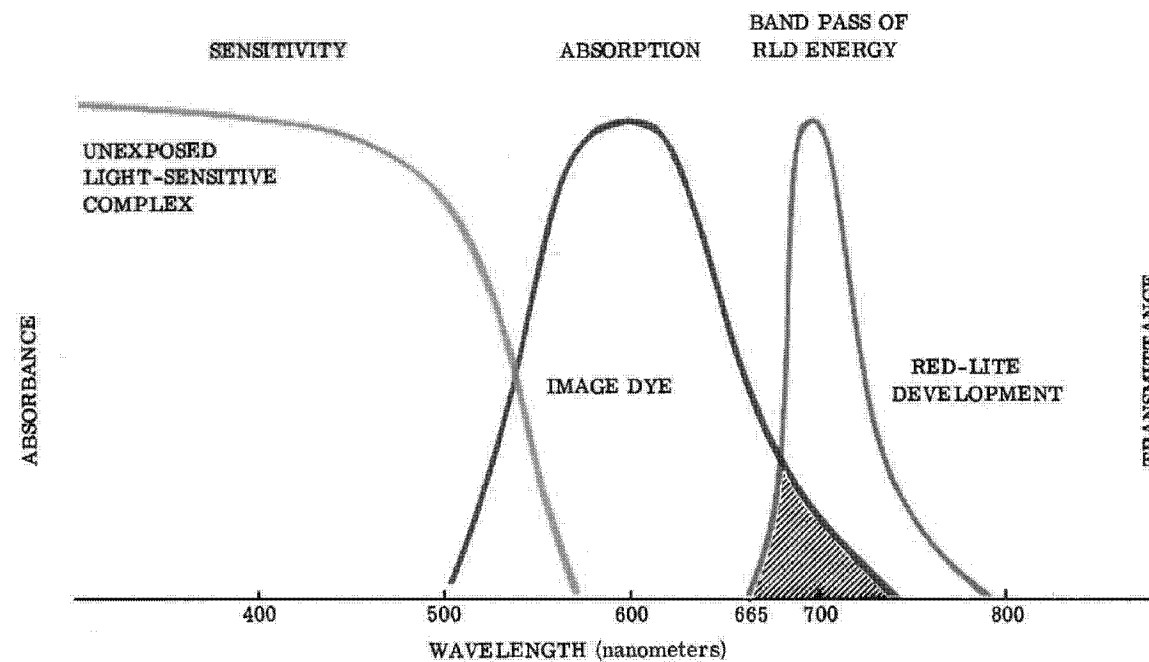
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## OPTICAL DEVELOPMENT PROCESS



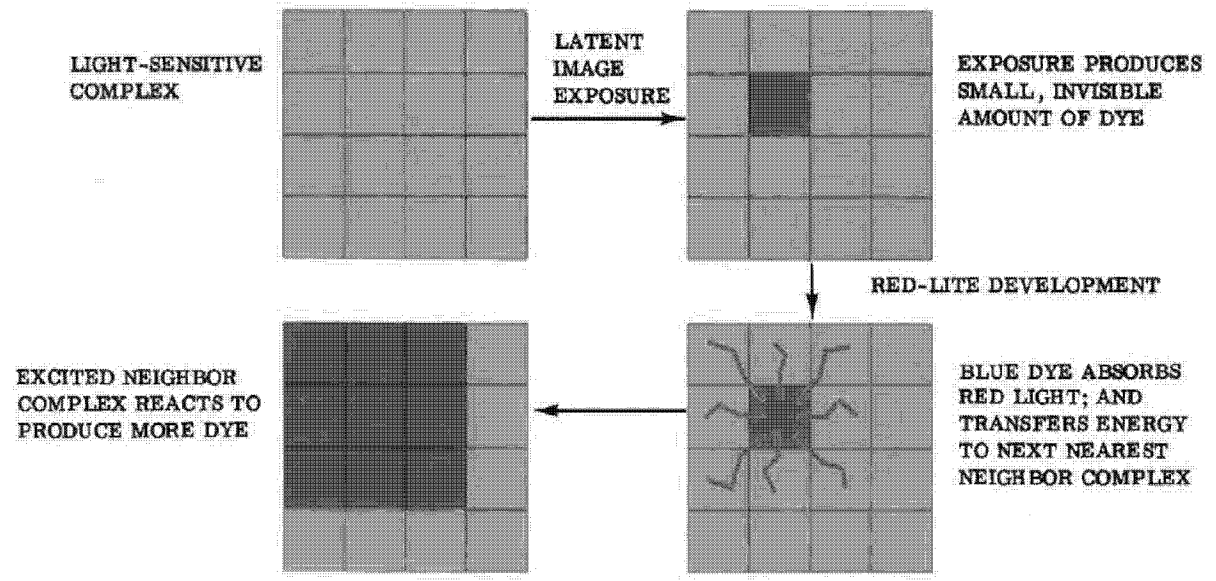
NOTE: The hash-marked area illustrates the red light furnished by a cut-off or band-pass filter selected to overlap absorption of image dye (blue) in a region of little or no absorption of a light-sensitive complex (yellow).

FIGURE 2-2

2-3

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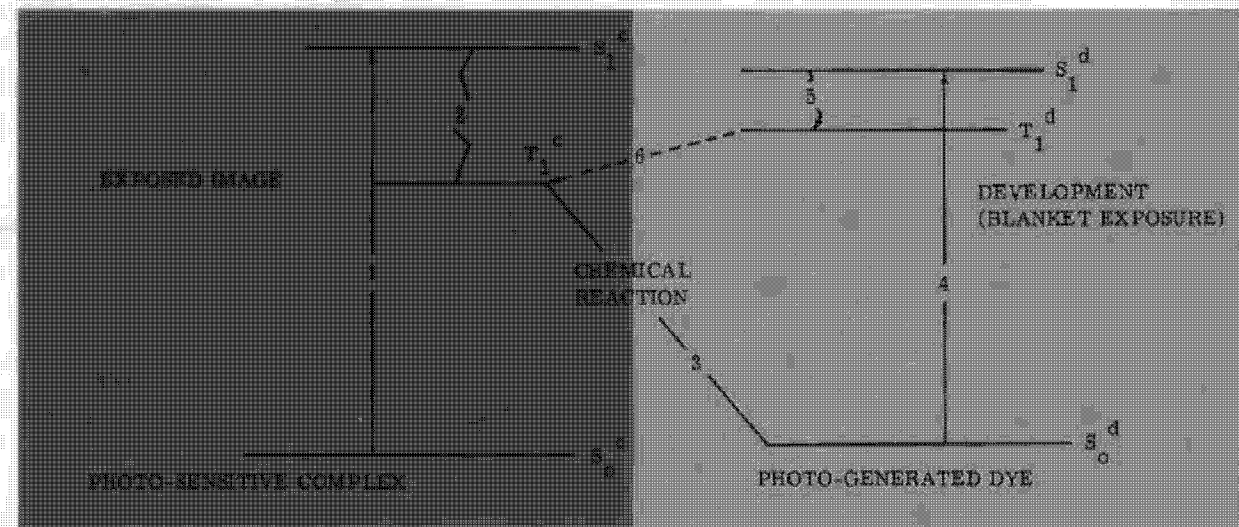
HOW OPTICAL DEVELOPMENT WORKS



NOTE: The molecular dimensions combined with the next nearest neighbor spatial requirements for energy transfer result in large amplification factors without measurable loss in resolution.

FIGURE 2-3

OPTICAL DEVELOPMENT POSTULATED MECHANISM



1. Light sensitive complex absorbs photon and raised to excited singlet state.
2. Excited singlet collapses to longer lived triplet state.
3. Triplet state of complex undergoes chemical reaction to produce dye.
4. Dye absorbs red light photon and raised to excited singlet state.
5. Excited singlet of dye collapses to longer lived triplet state.
6. Dye triplet at higher energy than complex triplet. Energy transferred to produce more complex triplet which subsequently produces more dye. (Step 3).

FIGURE 2-4

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wavelengths; the dye transfers this absorbing energy to a neighboring photo-sensitive complex which initiates the formation of additional dye molecules.

Once a visible image has been produced by RLD to the level required for the particular application, the film goes to a fixing step. The fixer (solvent rinse) is a liquid leaching process which selectively removes the unused activator and the dye former from the plastic film matrix. This selectivity allows removing the unused activator which, if not removed, would fog the film when exposed to room light. This process does not remove the visible dye already formed by the latent image exposure in the camera and the subsequent amplified dye image produced after the Red-Lite Development. The image dye is not soluble in the fixing solution, but the dye formers and activator are. A summary of the film composition, exposure, development, and fixing stages are presented in Figure 2-5.

The film is now capable of being handled in normal room light as would be the case with fully processed silver halide counterpart material.

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FREE RADICAL CHEMICAL PROCESS

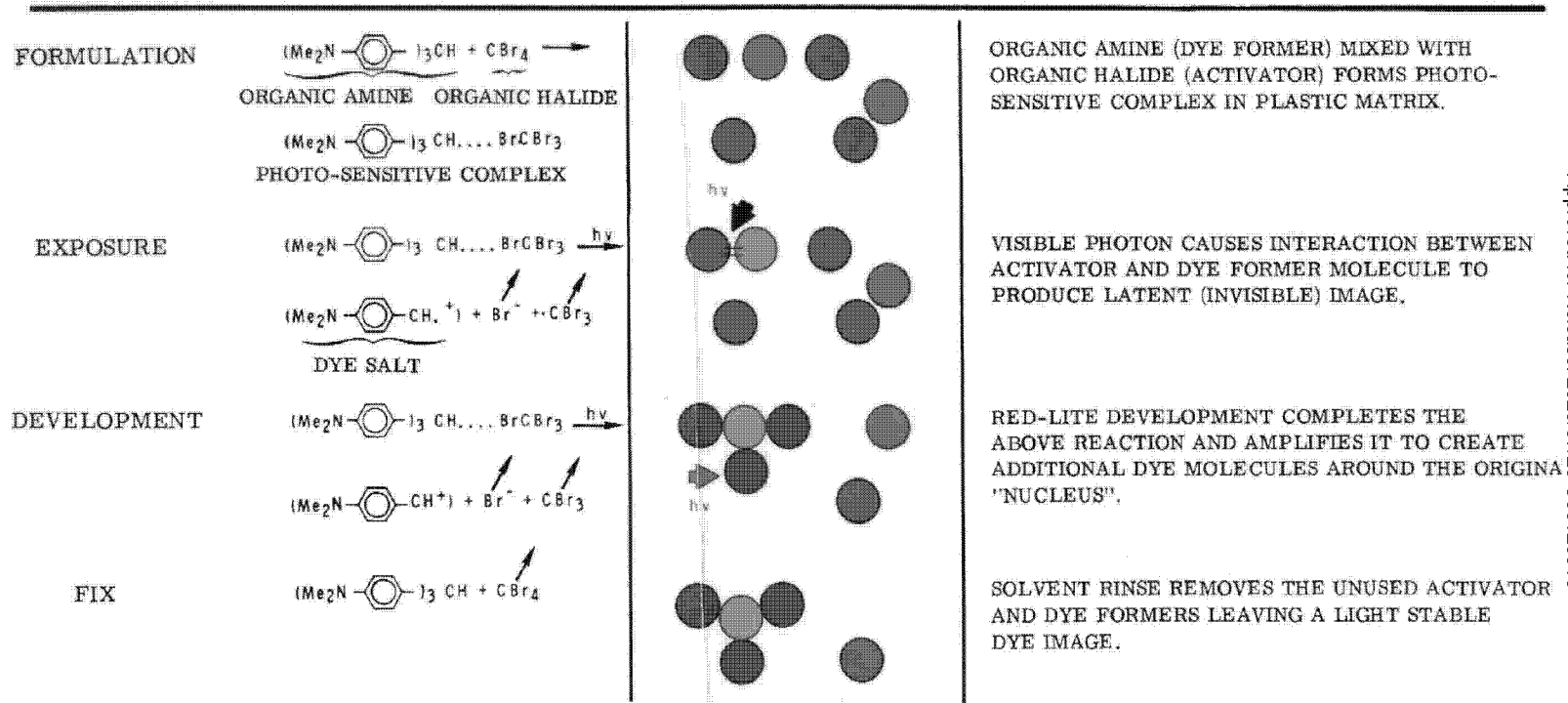


FIGURE 2-5

SECTION III

STATUS

3.1 INTRODUCTION

A significant milestone was achieved in the Free Radical Program in January 1974. It was demonstrated that it is possible to continuously coat short lengths of Free Radical Camera Speed Film on an Engineering Coater. To date, hand coatings have been the primary method for investigating many of the chemical and physical problems discovered during the past four years. Laboratory continuous-processing equipment is now being tested to provide not only continuous coatings of 70 mm by 250 foot lengths, but also the ability to Red-Lite Develop and solvent rinse (fix) these rolls on a continuous basis. The performance of the technology has shown and appears to have the capability of meeting the film specifications presented in Table 3-1.

TABLE 3-1  
FILM SPECIFICATIONS

<u>Characteristic</u>	<u>Specifications</u>
AFS Speed	9.0 (ASA $\approx$ 20)
Shelf Life (days)	Minimum required, $\geq$ 30 days with goal of 60 days at 70°F
Resolving Power (cycles/mm)	1000 cycles/mm at 2:1 contrast
Useful Sensitivity (nanometers)	400 to 660
Gamma Range	1.4 to 2.0
D <sub>min</sub>	$\leq$ 0.30
D <sub>max</sub>	Sufficient to produce useful log exposure range of 1.5

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This photographic system appears to be at least as critical in the formulation interactions as its silver counterpart. During the evolution of this system, each chemical change used to alleviate an area of poor performance has led to the reduction of performance in other critical areas. However, it has been possible each time to rebalance and solve these various interactions. What is emphasized here is that the performance of the Free Radical Imaging System is the result of a combination of many separate parts, each playing a role in securing the present or future performance. The detailed summary of current program status and problems is presented below.

### 3.2 LABORATORY CONTINUOUS COATINGS

During the period from December 1973 thru January 1974, over 150 coatings 10-15 feet long by 70 mm wide were made on the Engineering Coater. These were continuous coatings which included near simultaneous coating of both the photo-sensitive layer and the poly-vinyl alcohol (PVA) overcoat. These coatings demonstrated that the Free Radical Camera Speed Film is coatable on a reasonably repeatable basis. These coatings demonstrated film speeds near those specified and the desired sensitometric response, i.e., gamma, fog,  $D_{max}$ . Continuous coated films undergoing shelf life tests have shown no significant differences from previous hand coated samples. Many samples have exceeded 30 days shelf life and are still being tested. The important aspect of the Engineering Coater is that this now gives us an ability to make Free Radical Film of reasonable quality with a minimum of scratches, voids, pinholes, etc. The ability to produce reasonable quality films even in limited quantity will allow a considerably greater evaluation of the film characteristics. It should be emphasized, however, that these coatings are not production quality. This step is one that is prior to even the development of pilot coatings.

### 3.3 SENSITOMETRIC RESPONSE

The overall sensitometric response of the film indicates that the contract specifications can be met. The Engineering Coater has produced AFS values of 9.0. The latest shelf life tests are showing little speed loss with Formula 15 Tests approaching one month's storage at room temperature. Figure 3-1 illustrates typical film data from the Engineering Coater. These curves are not intended to show the longest shelf life or highest speed the film is capable of, but just an example of the latest results. Testing is still underway with films made at the same time. That is, the ultimate shelf life of Formula 15 is yet to be determined. Curve C illustrates the highest speed Formula 15 coating seen to date; however, film speed is not considered a significant problem at this point in the program. Speeds near to or equal to the contract specification have been obtainable for the last two years. Unfortunately, every time some aspect of the formula or the coating changes, speed usually drops and

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TYPICAL RESULTS OF CURRENT FORMULA COATINGS

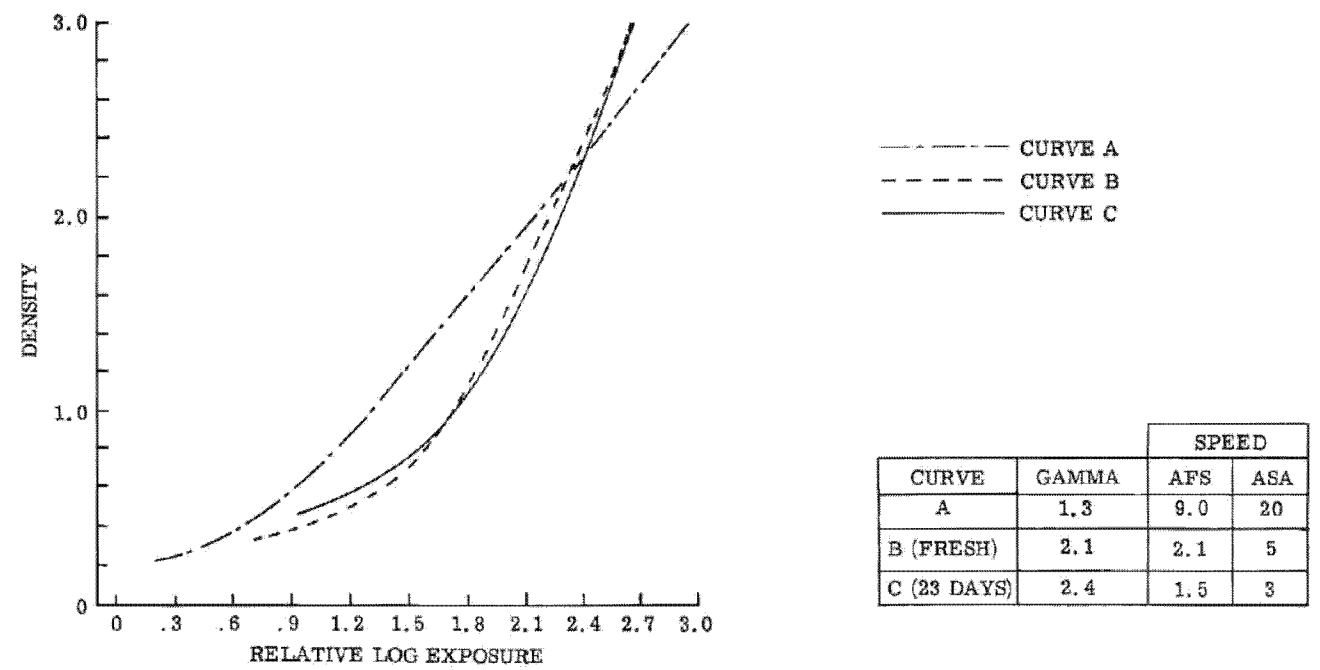


FIGURE 3-1



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then readjusts as the change is optimized. The formula has never been stable enough during the R&D program to enable spending sufficient time studying the "ultimate" speed capability of the Free Radical Film System. The current formula, however, is close enough to optimum to enable it to be coated on the continuous Engineering Coater.

The work over the past two years, which includes the continuous coatings, clearly indicates that the desired gamma,  $D_{\min}$ , and  $D_{\max}$  requirements have been achieved.

In summary, the sensitometric specifications of this film are reasonable and can be achieved. It is felt, therefore, that this will not be a problem in future developments.

### 3.4 IMAGE QUALITY (RESOLVING POWER)

Extensive resolving power testing of the various formulas has shown values on the order of 800 to 1,200 cycles/mm at a 1.6:1 contrast regardless of the formula. To date, no relationship has been found between the film speed and resolving power, although one must certainly exist. Theoretical computations at Horizons indicate that the resolving power of this film will not be adversely affected until the film speed approaches an AFS value of approximately 200 to 300. Figure 3-2 illustrates a Threshold Modulation (TM) Curve comparison between 1414 and Free Radical which shows that Free Radical Film has superior imaging characteristics. Figure 3-3 graphically shows the difference in imaging characteristics between 1414, 3400, and Free Radical Film types. The basic molecular nature of this film insures a capability to provide the resolutions desired. There are some practical problems, however, which are discussed later in this report.

An interesting phenomena has been observed which indicates that image formation in the photo-sensitive layer of this Free Radical Film may be unique. Experiments have indicated that the image is not formed on the surface, middle, or lower regions of the film, but appears to build in a unique straight line through the film (top to bottom) resulting in very high sharpness even at the resolution limit. This indicates that Free Radical Film does not exhibit the usual light scattering associated with silver halide films.

### 3.5 SHELF LIFE

Shelf life has been one of the primary areas of concern since the inception of this development program. Early versions of a camera speed film had a shelf life on the order of minutes. Usually after 15 minutes, the photographic system was completely dead. Investigations determined that the cause of the speed decay with time was twofold. First, the carbon tetrabromide activator rapidly sublimated out of the sensitive layer;

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# THRESHOLD MODULATION COMPARISON BETWEEN 1414 AND FREE RADICAL FILMS

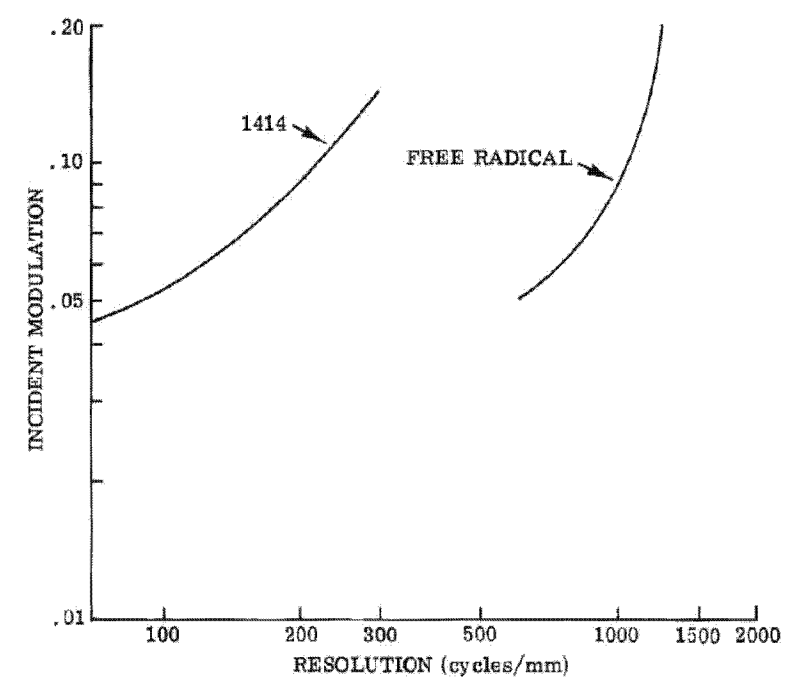


FIGURE 3-2

3-5

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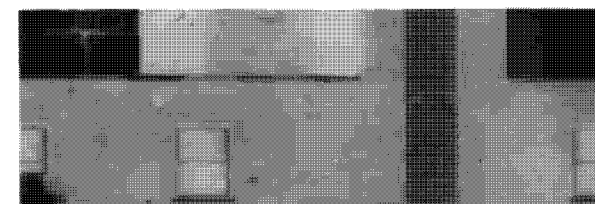
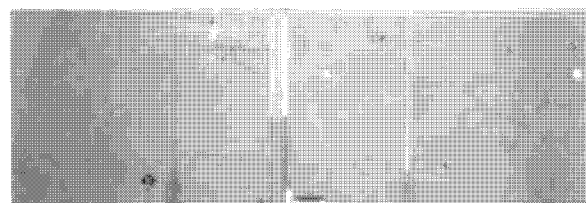
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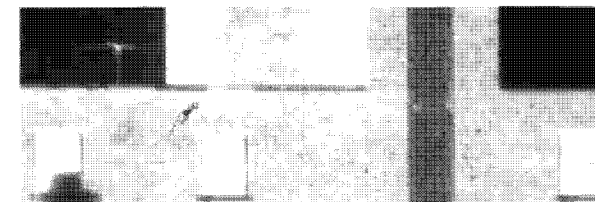
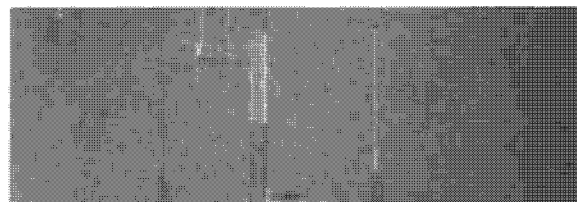
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# IMAGE QUALITY COMPARISONS UTILIZING ANTENNA AND BUILDING

FREE RADICAL FILM TYPE



1414 FILM TYPE



3400 FILM TYPE

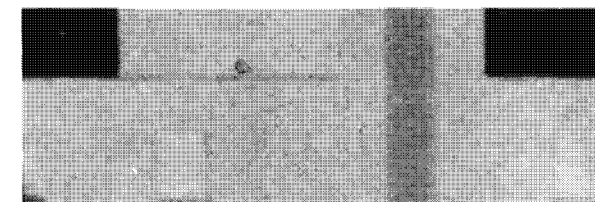
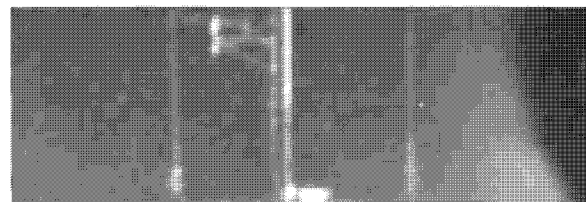


FIGURE 3-3

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and secondly, oxygen in the air apparently caused the formation of hydro-peroxides which causes a cessation of the image formation chain reaction. Both of these problems were solved by the use of a PVA overcoat.

While the overcoat solved the rapid speed decay problem, the ultimate shelf life of the Free Radical Film has yet to be determined. Hand coatings with overcoats were very unsatisfactory for shelf life testing. Any physical defect (pinholes, dust, dirt, etc.) in the coating causes non-image density buildup making the test results marginal at best. However, it should be noted that the best shelf life attained with this mode of testing was 50 days. The Continuous Coater will provide considerably improved quality coatings, and should allow for more extensive testing of the film's shelf life capability. The other obvious difficulty in running tests of this length is that the evaluation takes the same amount of time, i. e. , it takes six months to determine if the film has a six month shelf life.

### 3.6 PANCHROMATIC SENSITIVITY

The inherent sensitivity of the Free Radical Camera Speed Film System is in the UV, blue, and green regions of the spectrum. In order to make a useful camera film, spectral sensitivity must be increased to 660 nanometers. The possibility of sensitizing to this region was demonstrated in 1971. Work was delayed, however, so that other key problem areas could be accomplished, i. e. , shelf life at 70° F, etc.

During the past six months, work on pan sensitivity was resumed at a low level. Again, it was demonstrated that the Free Radical System can be sensitized to 660 nanometers and beyond, and that the process to secure pan sensitization closely follows that of silver halide systems.

From these hand coating trials, work will now concentrate on continuous coatings. The effect of pan sensitivity on shelf life, AFS speed increase, and the interaction of pan sensitivity with the optimum cut on wavelength for Red-Lite Development must still be investigated.

There appears to be no major obstacle in securing the required pan sensitivity with continuous coatings since the mechanism has already been demonstrated in the static case. The problem, however, is the possible interference with Red-Lite Development.

### 3.7 RED-LITE DEVELOPMENT (PROCESSING)

Several hypotheses have been postulated to explain the mechanism of Red-Lite Development; these employ the classical Jablonski Energy Transfer Mechanism. Although the mechanism of RLD is not absolutely defined, this area, as others, has been handled in a pragmatic fashion. It is impossible to separate the evolution of the processing equipment from the fundamental mechanism, for it has been through the evolution of this equipment that the high speed and uniformities of processing have been obtained. The processors have evolved from very small laboratory

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breadboards to more sophisticated sheet film laboratory processors to a 70 mm continuous roll processor. The efficiency of RLD has been markedly improved. This generation processor brought power requirements down and improved the overall uniformity of processing.

### 3.8 FIXING EQUIPMENT

Fixing is also known as solvent rinsing. Fixing removes the unused activator and makes the processed image "permanent." This equipment has progressed from a tray with fixing solution to a continuous solvent rinse breadboard which is capable of processing lengths of 70 mm film at speeds up to five feet per minute.

### 3.9 ACCOMPLISHMENT MATRIX

Table 3-2 on page 3-9 provides a summary of the film development status and forecasted goals.

### 3.10 CURRENT DEVELOPMENT PROBLEMS

While the development effort to date has been extremely successful, problems remain to be solved before a final usable film can result. These problems are:

#### A. Density Increase Under Overcoat After Exposure

This problem has intermittently plagued the program. It is manifested, only after an image forming exposure, by a gradual increase in density and an attendant loss of resolution if the overcoat is left on. This problem becomes most severe after approximately an hour. There is no problem if the overcoat is removed and the image processed. The practical severity of the problem is obviously a function of whether or not the user can remove the overcoat immediately after exposure. The cause of this problem is currently unknown. The project personnel hope to determine the cause and be able to resolve this problem by the end of March 1974.

#### B. Shelf Life

Paragraph 3.5 discussed the problems with testing the shelf life of this film. Not only have the tests been hampered by the poor quality of the hand coatings, but shelf life tests can be very time consuming. The problem is that the ultimate shelf life capability of this film system is not known.

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TABLE 3-2

PROJECT ACCOMPLISHMENTS AND FORECASTED GOALS

<u>Date</u>	<u>Type of Coating</u> <u>Size</u>	<u>Speed</u> <u>(AFS)</u>	<u>Shelf Life</u> <u>at 70° F</u> <u>(days)</u>	<u>Resolving</u> <u>Power</u> <u>(cycles/mm)</u>	<u>Useful</u> <u>Sensitivity</u> <u>(nanometers)</u>	<u>Gamma</u> <u>Range</u>	<u>D<sub>min</sub></u> <u>D<sub>max</sub></u>	<u>Type of</u> <u>Processing</u>
30 June 1973	4"x5" Sheets Hand Coatings (maximum useful area)	4.5	30	>1000 at 1.6 : 1 contrast	N. A.	1.4 to 2.0	.30 Meets Specs	Sheets 1" x 1 1/2" Process Capability
31 Jan 1974	10' x 70 mm Continuous Laboratory	3.0	30*	>1000 at 1.6 : 1 contrast	N. A.	1.4 to 2.0	.30 Meets Specs	Sheets 4" x 5" Process Capability
		9.0	14*		N. A.	1.4 to 2.0	.30 Meets Specs	
Forecast by 1 July 1974	250' x 70mm Continuous Laboratory	≥ 10.0	≥ 30 with goal of 60 days	1000 at 2: 1 contrast	400 to 660	1.4 to 2.0	≤ 0.30 Sufficient to Produce ULE of 1.5	250' x 70 mm Roll Continuous

NOTE: The asterisk (\*) denotes that the shelf life continues to be stable; additional samples will be taken until the film supply is depleted.

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C. Spectral Sensitization

There appears to be no problem in obtaining the desired spectral sensitization of the Free Radical Film. The problem is the currently unknown effect this will have on the Red-Lite Development Process. The RLD Process currently operates with a cut on wavelength of ~680 nanometers. Pan sensitization could have a portion (tail) in this region that would make the RLD very critical and difficult to control. At worse, it could cause spontaneous fog. It is possible, however, that with pan sensitization, the "development tail" will move into the near infrared region making the problem disappear. Whether or not this is a problem will not be determined until this additional spectral sensitivity is introduced into RLD films. It is felt that a better understanding of the impact of spectral sensitivity should be achieved within the next few months.

D. Materials Scale-Up.

Some of the critical areas which must receive attention in the next six months are associated with the scale-up to a pilot coating. These would primarily be the materials scale-up from laboratory synthesis, and the purification methods to reasonable levels of quantities and processes having significantly greater yields than are presently found in laboratory-size preparation. Large supplies of quality ingredients could be a problem.

E. Subbing

Demonstrations of performance evaluation, whether on hand coatings or laboratory continuous coatings, have been on materials without a subbing layer. A subbing layer must be provided within the next few months in order that a total film package will be available for a roll film test. What effect a subbing layer will have on the photo-sensitive layer, and what problems this will cause, is unknown at this time.

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SECTION IV

FUTURE

4.1 SUMMARY

The following summarizes the projected goals for the Spring of 1974:

- A. Produce 70 mm x 250' rolls of film for test and evaluation.
- B. Establish the following film characteristics.

<u>Characteristic</u>	<u>Specification</u>
AFS Speed	$\geq 10.$
Shelf Life (days)	Minimum required $\geq 30$ days, goal of 60 days
Resolving Power (cycles/mm)	1000 cycles/mm at 2:1 contrast
Useful Sensitivity (nanometers)	400 to 660
Gamma Range	1.4 to 2.0
$D_{min}$	$\leq 0.30$
$D_{max}$	Sufficient to produce useful log exposure range of 1.5

4.2 IMMEDIATE GOALS

The current program plan calls for having a Pilot Production Facility on-line early in 1976. This would provide for reasonably significant quantities of Free Radical Film for extensive system testing in the Summer of 1976. To attain this goal, the following important steps will be required.

4.2.1 Pilot Coating Facility

Initial design work has begun on a pilot coater. A decision to proceed with fabrication of such a coater will be based on the demonstrated ability to solve the key problems by that time. The Pilot Coating Facility itself could be a problem, as going from laboratory to pilot production



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coatings is not an easy task.

#### 4.2.2 Film Testing

Before any film can be used in an operational system, extensive testing will have to be accomplished. This testing will consist of both photographic and physical tests. Repeatability of sensitometry with many coatings, resolving power, and MTF response all will have to be intensively evaluated. In addition, investigations on the physical characteristics and behavior of the film will have to be accomplished. The integrity of such a film in a flight stack, as well as whether or not this film can be intermixed with silver halide films must be studied.

Another important study that needs to be undertaken is the nature of the dye image. There are few, if any, dye images which exhibit either the neutrality or the permanency to various types and levels of radiation that a totally processed and fixed silver image can. Although the dye image of these films provides the possibility of manipulating the printing contrast through use of color filtering, some attention must be placed on testing to determine the actual resistance of the dye image to various types of illumination, and what the effects on the image are of repetitive printing for duplication purposes. It may be necessary to add dye stabilizers to the formula. The effect of these on the photographic properties is unknown.

#### 4.2.3 Elimination of the Overcoat

One of the longer range goals is to eliminate the need for the overcoat. This would involve the use of a less volatile activator, and hence, would provide a greater shelf life. While there are no plans to eliminate the overcoat before going to a pilot coating, an investigative study will be undertaken within the next one to two years.

### 4.3 CONCLUSIONS

A. Free Radical Camera Speed technology has exhibited many characteristics, which, even under the laboratory development phase, appear to be useful for application in high resolution imaging systems.

B. It is extremely important to note that this technology is presently in the stage of transitioning from the laboratory to continuous coatings. Pilot production coatings of this film are still in the future.

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C. There have been many accomplishments as well as many problems within the initial stages of development. These have been handled on a pragmatic step-by-step basis. There are still known problems to be solved and certainly unknown problems will occur which will impede progress to establishing a usable film.

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