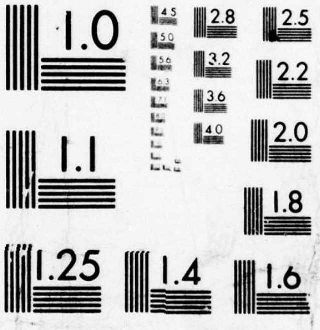
AD-A055 013 ARMY ENGINEER TOPOGRAPHIC LABS FORT BELVOIR VA F/G 14/5
REVIEW OF PHOTOSENSITIVE MATERIALS FOR HOLOGRAPHIC RECORDINGS.(U)
APR 78 J W GLADDEN

UNCLASSIFIED ETL-0128 NL

1 OF 1
AD
A055013

END
DATE
FILMED
7-78
DDC


1.0
4.5
5.0
5.6
6.3
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

12

ETL-0128

# Review of photosensitive materials for holographic recordings

JAMES W. GLADDEN

APRIL 1978

U.S. ARMY CORPS OF ENGINEERS
ENGINEER TOPOGRAPHIC LABORATORIES
FORT BELVOIR, VIRGINIA 22060

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

ETL

# ERRATA SHEET

ETL REPORT NO. ETL-0128

## Review of Photosensitive Materials for Hologrpahic Recordings

Page 10, line 4: After the word film add a comma.

Page 10, line 30: Change the word of to read or.

Page 10, footnote 7: Change 1955 to read 1975.

Page 11, line 7: After the word reaction add a comma and ... but for a photoreaction to occur in a light struck material, there must be absorption of the light by the material.

Page 11, line 11: Change $10^{12}$ to read $10^{-12}$ .

Page 11, line 12: Change $8.3\text{x}10^{1}$ to read $8.3\text{x}10^{7}$.

Page 17, line 26: Change 11B to read IIB.

Page 18, lines 26 & 27: Change poly-N-vinylcarbaxole to read poly-N-vinylcarbazol

Page 20, line 19: Change consisting to read consists.

Page 39, line 11: Delete the word By.

Page 43, line 27: Change $SO_3N_2^-$ to read $SO_3N\bar{a}$.

Page 51, line 14: Change in to read is.

Page 62, line 15: After the bracket add...less than.

Page 62, line 19: After intensities add...greater than.

Page 67, line 22: After centimeter add...are.

Page 67, line 36: Change from to read form.

Page 74, lines 2 & 3: Change photo to read photon.

Page 81, line 8: Change 1955 to read 1975.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

(14)

1. ~~REPORT NUMBER~~
ETL - 0128

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
(6) REVIEW OF PHOTOSENSITIVE MATERIALS
FOR HOLOGRAPHIC RECORDINGS.

5. TYPE OF REPORT & PERIOD COVERED
(9) Technical Rep[redacted]t.

6. ~~PERFORMING ORG. REPORT NUMBER~~

7. AUTHOR(s)
(10) James W. Gladden

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U.S. Army Engineer Topographic Laboratories
Fort Belvoir, Virginia 22060

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
(16) 4A161102B52C

11. CONTROLLING OFFICE NAME AND ADDRESS
U.S. Army Engineer Topographic Laboratories
Fort Belvoir, Virginia 22060

12. ~~REPORT DATE~~
(11) Apr[redacted]78

13. NUMBER OF PAGES
84

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified
(12) 87p.

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

DDC
RECEIVED
JUN 12 1978
F

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Holography
Holographic Recording Materials
Photosensitive Materials
Electrostatic Imaging Materials
Photoresists
Diazos
Diazo-Oxides
Azides
Diazo Gelatin
Dichromated Gelatin
Photochromic Materials
Photopolymers
Bleached Silver Halide Holograms

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

There is a program objective to systematically evaluate photosensitive recording materials that can be used in holographic and other coherent optical systems. In association with this, a detailed literature search was undertaken in which considerable information was obtained and compiled in this report. However, the recent literature describing the recording materials, particularly the nonsilver recording materials, is often confusing

continued

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

403 192

20. continued

or incomplete. Very little detail is given about the chemistry, mechanisms, and processes of these materials with a view toward developing particular materials for use in holography. An objective of this report is to describe these aspects of the recording materials in a way that will aid in their future development and use in holography.

Over 100 references were reviewed that treat electrostatic imaging materials, photoresists, hardened dichromated gelatin, photopolymers, photochromic materials, and bleached silver halide materials. Subcategories include Scott Graphics TEP film; photoplastic film; diazos, diazo-oxides and azides; Shipley's AZ 1350 positive photoresist; Hughes-NRC, DuPont and Bell Laboratories photopolymers; photochromic lithium niobate; and different halide bleaches for silver halide bleached holograms.

The report compares a number of the characteristics of the different classes of holographic recording materials. Problems associated with the recording materials are described, and those material properties that enable use in important applications are pointed out. The not too well known chemistry of certain well known recording materials is also described.

| | |
|---|---|
| ACCESSION for | |
| NTIS | White Section ☑ |
| DDC | Buff Section ☐ |
| UNANNOUNCED | ☐ |
| JUSTIFICATION | |
| BY | |
| DISTRIBUTION/AVAILABILITY CODES | |
| Dist. | SPECIAL |
| A | |

# SUMMARY

This report reviews and assesses photosensitive materials with potential applications in holographic recordings. Over 100 references treat electrostatic imaging materials, photoresists, hardened dicromated gelatin, photopolymers, photochromic materials, and bleached silver halide materials. Subcategories discussed include Scott Graphics TEP film, photoplastic film, diazos, diazo-oxides and azides, Shipley's AZ 1350 positive photoresist, Hughes-NRC, DuPont, and Bell Laboratories photopolymers, photochromic lithium niobate, and different halide bleaches for silver halide bleached holograms. The report describes the chemistry, mechanisms, and processes of these materials in terms of developing particular photosensitive materials for use in holography.

Specifically, the report shows that silver halide photosensitive materials are unique among the population of photosensitive materials. Using silver halide Lippmann emulsions in off-axis holography is prompted by the greater spectral sensitivity, photosensitivity, and familiarity of processing, at the same time possessing the capability of recording the high spatial frequencies used in holography. The electrostatic imaging processes are the only class of photographic processes whose photosensitivity more nearly equals that of the Lippmann emulsions. An example is the photoplastic materials. The photoplastic materials are capable of recording spatial frequencies on the order of 1000mm$^{-1}$ in the production of phase, surface holograms.

The photoresists are a class of photosensitive materials that are among the least photosensitive. Very high spatial frequencies may be recorded in thin layers of positive photoresists as phase, surface variations. The photoresists have enabled development of RCA's holographic moving map display, low scatter holographic gratings for use in the vacuum ultraviolet, and iron oxide holograms with excellent dimensional stability to changes in ambient temperature and percent relative humidity.

The hardened dichromated gelatin plate produces holograms well known for their high diffraction efficiency and signal-to-noise ratio. In reviewing the patent literature, the use of dichromated gelatin emulsion has been replaced by the diazos, diazo-oxides, and azides in photolithography because these types of photosensitive materials have sufficient shelf-life stability to permit commercialization. Perhaps the first of the improved shelf-life materials used in holography is the Shipley AZ 1350 positive photoresist. The photopolymers have greater photosensitivities than the photoresists, but not as great as the silver halide emulsions. The phase-type holograms are produced by a completely dry and rapid processing. Modulations in refractive indices are found either on the surface or in the bulk of the layer. Although the photochromic materials are among the least photosensitive materials, they are capable of extremely high spatial frequency recordings. Dry processing enhances the use of this recyclable material.

The bleached silver halide holograms have problems associated with wet development, archival properties, and emulsion stability. Interest in nonsilver photosensitive

processes is prompted by the problems inherent in the silver halide processes. For example, there are nonsilver processes with completely dry development and processing, with excellent shelf life for the photosensitive materials and archival quality for the holograms, and with dimensional stability to changes in ambient temperature and percent relative humidity built into the image-forming layer. In addition, there are nonsilver processes that have applications in areas not permitted by the silver halide processes. This is seen in methods that produce holograms of colored maps, rapidly using embossing techniques in thermoplastics and in the production of holographic gratings for use in vacuum ultraviolet.

# PREFACE

This work was authorized by the U.S. Army Engineer Topographic Laboratories, Fort Belvoir, Virginia under DA Project 4A161102B52C entitled "Research in Geodetic, Cartographic, and Geographic Sciences."

A literature review of the nonsilver photographic materials with a degree of suitability for off-axis holography was undertaken. The silver photographic materials are treated more generally. Where possible, applications for the different holographic recording materials to specific recording problems are treated. It is planned that supplements will be added to this literature review that will include additional silver and nonsilver photographic materials.

# CONTENTS

## ILLUSTRATIONS

# REVIEW OF PHOTOSENSITIVE MATERIALS FOR HOLOGRAPHIC RECORDINGS

## INTRODUCTION

PURPOSE OF STUDY. Since 1970, the U.S. Army Engineer Topographic Laboratories (ETL) has supported research in coherent optics applied to mapping. Since one aspect of this research is to evaluate photosensitive recording materials that can be used in holographic and other coherent optical systems, ETL is developing and is improving on a capability to test selected holographic recording materials that may be useful for holographic storage. A detailed literature search was conducted. This search provided considerable information about holographic recording materials and that information is compiled in this report.

An intimate connection exists between the photosensitive recording medium and the quality of a hologram. However, recent literature describing the recording materials (particularly nonsilver recording materials), is often confusing or incomplete. For example, very little information is given about the aspects, i.e. the chemistry, mechanisms, and processes, of these materials as applied to their possible use in holography. This report describes these aspects of the materials and is intended to aid in their development.

SCOPE OF THE REPORT. The report describes those photosensitive materials referred to as holographic recording materials that offer a degree of suitability for off-axis holography. The report organization consists of an Introduction, the sections that discuss six different classes of recording materials, a Review and Conclusions. The nonsilver recording materials are described in detail regarding process mechanisms, chemistry, preparation methods, and image recording. The silver recording materials are treated more generally because of the large volume of commercial materials available and the greater familiarity that Researchers have with these materials. Where possible, applications for the different holographic recording materials are related to specific recording problems. An evaluation is offered describing the suitability of different recording materials for off-axis holography and indicating how the materials may be improved. Over 100 references are given that include many patents not mentioned in earlier review articles.

Although this report discusses six different classes of holographic recording materials, other types do exist. However, the recording materials selected for this review either offer the most promise for storage of topographic information in the near future or have a particular advantage in hologram properties, storageability of materials, or uniqueness in application. Future supplemental reviews are expected to be prepared that would include silver halide amplitude, 3M dry silver, vacuum-deposited silver halide, additional photochromic materials (e.g. photochromic spiropyran in styrene polymer; nickel, molybdenum-doped calcium titanate; and iron, molybdenum-doped strontium titanate), the ferroelectric crystals and ferroelectric photoconductor devices, the amorphous semiconductors, photochemical etching of silicon and germanium films, bismuth thin films, Kalvar vesicular films, photodegradable thermoplastics, Technifax diazotype film type D8-402, Horizons Research styryl free-radical film, 3M thermatone film type 7889, and the alkali halides. These reviews will be prepared when evaluation of these materials becomes important to the in-house work.

PREVIOUS REVIEW ARTICLES. Seven review articles of holographic recording materials discuss major classes of recording materials in general and give some insight into their holographic parameters and photosensitive properties. The first of these, John C. Urbach's review, very neatly classifies the different recording materials according to their ability to form thin or thick, amplitude or phase holograms.[1] Subclassifications according to reflection or transmission types are discussed in the article. Also, there is a discussion of materials for use in infrared and ultraviolet holography. A chapter in Robert J. Collier's book describes holographic properties of silver halide emulsions, dichromated gelatin films, photoconductor thermoplastic (so called photoplastic) films, photochromic materials and ferroelectric crystals.[2] Collier also describes the method of hologram formation, exposure and sensitivity, recording resolution, noise, recording linearity, and exposure characteristics observed with holograms.

An entire issue of ***RCA Review*** describes many exotic materials for holographic recording.[3] Different articles discuss holographic storage in lithium niobate, transition metal-doped lithium niobate, dichromated gelatin, thermoplastic (also called photoplastic), photochromic calcium fluoride, stronium titanate, and calcium titanate crystals. Other articles in the ***RCA Review*** discuss holographic information storage, redundant holograms, recyclable holographic storage media, and the RCA holotape.

The U.S. Air Force published a report by W. S. Colburn ***et al.*** in January 1973.[4] In this report, the materials reported on for hologram preparation are bleached photographic emulsions, dichromated gelatin, photopolymer, photodegradable thick thermoplastic, photoresist and photoresist with iron oxide, and photoplastic layers. These all

---

[1] **John C. Urbach, "Advances in Hologram Recording Materials,"** ***Proceedings of the Society of Photo Optical Instrumentation Engineers,*** **Vol. 25, April 1971, pp. 17-41.**

[2] **R.J. Collier, C.B. Burckhardt, and L.H. Lin, "Hologram Recording Materials,"** ***Optical Holography,*** **Academic Press, New York, 1971, Chapter 10.**

[3] **R.F. Ciafone, Ed. "Optical Storage and Display Media,"** ***RCA Review,*** **Vol. 33, No. 1, March 1972.**

[4] **W.S. Colburn, R.G. Zech, and L.M. Ralston,** ***Holographic Optical Elements,*** **Technical Report AFAL-TR-72-409, Wright-Patterson Air Force Base, Ohio, January 1973.**

form phase type holograms.

Richard G. Zech published a technical report for the U.S. Air Force,[5] and a doctoral dissertation.[6] Described in the technical report are hologram recordings in Horizons Research Inc. LHS7 photoresist and their styryl free-radical film Scott Graphics TEP film, a photoplastic film, Kalvar vesicular film, a Technifax diazo type D8-402 film, a 3M type 7859 dry silver film and their type 7889 thermatone film. Other unconventional recording materials treated in the report are amorphous semiconductors, vanadium oxides, arsenic trisulfide, bismuth films and photochemical etching. Described in the doctoral dissertation is holographic recording in photodegradable thermoplastics consisting of sensitized polymethyl methacrylate or cellulose acetate butyrate, photoresist (Horizons LHS7), photographic emulsions (Kodak 649F and the Agfa Gevaert emulsions), and also hardened dichromated gelatin although it was not an important material in the study.

The most recent review article of holographic recording materials was prepared by Robert L. Kurtz and Robert B. Owen.[7] The review develops a concept of an ideal holographic recording material and briefly describes the commercially available silver halide plates and films, the photoresists, the photopolymers, Horizons Research Incorporated styryl free-radical film, Scott Graphics TEP film, and other noncommercial materials such as photoplastics, dichromated gelatin, photochromics, and electro-optical crystals. Also, the article contains tables depicting applications for the recording materials and a categorized bibliography with 93 entries of the more recent reports, articles, and books on the subject of holographic recording materials.

In general, these review articles describe a group of now very familiar holographic recording materials and their photographic and holographic parameters. Still, very little detail is given about the chemistry, mechanisms, and processes of these materials with a view toward developing particular photosensitive materials for use in holography.

BACKGROUND. This section describes fundamentals that are used in the report.

That light can produce chemical changes of photolysis in materials has been known for many years. Since chemical change is denoted by breaking and forming chemcial bonds, the light then interacts in some way with the electrons that are in

---

[5] **R.G. Zech, *Holographic Recording Materials,* Technical Report, F 30602-74-C-0030, Rome Air Development Center, Griffiss AFB, New York, July 1974.**

[6] **R.G. Zech, *Data Storage in Volume Holograms,* Doctoral Dissertation, University of Michigan, 1974.**

[7] **Robert L. Kurtz and Robert B. Owen, "Holographic Recording Materials-A Review," *Optical Engineering,* Vol. 14, No. 5, September - October 1955, P. 73.**

bond formation. Thus, photochemical reactions involve electronic transitions in molecules, and nearly all those electronic transitions occur in the ultraviolet and visible region of the electromagnetic spectrum. Further, the Grotthus-Draper law permits only photochemical reactions to occur by light that is absorbed by the molecules. For a photochemical reaction to occur in a light-struck material, there must be absorption of the light by the material; however, not all light that is absorbed by a photosensitive compound produces a photochemical reaction. The extent to which light is absorbed in different materials is determined with techniques in abosrption spectroscopy.

Silver halide materials are unique among photosensitive materials in that the photosensitive unit is a silver halide crystallite, that is, a minute crystal. A silver bromide crystallite that has a volume of $10^{12}$ cubic millimeters is composed of about $8.3 \times 10^{7}$ molecules. This would be a crystallite in a fine-grained emulsion. The absorption of 4 to 25 quanta per crystallite produces conversion of the entire crystallite in development into a grain of metallic silver, an image unit, that is the smallest unit that comprises the imaging material. The conversion is accomplished with great amplification of the amount of light absorbed by the crystallite, and it is this property of silver halide materials that produce their very high sensitivity. Upon photolysis, most photosensitive materials produce image units that have molecular dimensions with the absorption of each quantum of actinic light. Others may produce image units comprised of hundreds to thousands of molecules with the absorption of a single quantum of actinic light. These photosensitive materials do not exhibit the photosensitivity of the silver halide materials; however, they may not be limited to the recording resolutions of the silver halide that typically have larger image units.

That the resolution capability of the recording material is important to off-axis holography is seen in the very high spatial frequencies that are recorded in these holograms. The recorded spatial frequency is dependent upon (1) the angle that the two coherent beams of light make at the recording plane (figure 1) and (2) the wavelength of light used. If the bisector of the angle that the two beams make in air is normal to the recording plane, then one-half of the interbeam angle is defined as $\theta_a$. The spatial frequency, $\nu$, may be calculated from the following relationship:

$$\nu = \frac{1}{d} = 2\,\frac{\text{Sin}\,\theta_a}{\lambda_a}$$

d is the distance between corresponding regions in the interference pattern, and $\lambda_a$ is the wavelength of the coherent light in air. Because of refraction that occurs as the light enters the recording medium, $\theta_a$ and $\lambda_a$ become $\theta_m$ and $\lambda_m$. Then, with Snell's law

$$\frac{\text{Sin}\,\theta_a}{\lambda_a} = \frac{\text{Sin}\,\theta_m}{\lambda_m} \quad \text{and} \quad \nu = 2\,\frac{\text{Sin}\,\theta_m}{\lambda_m}$$

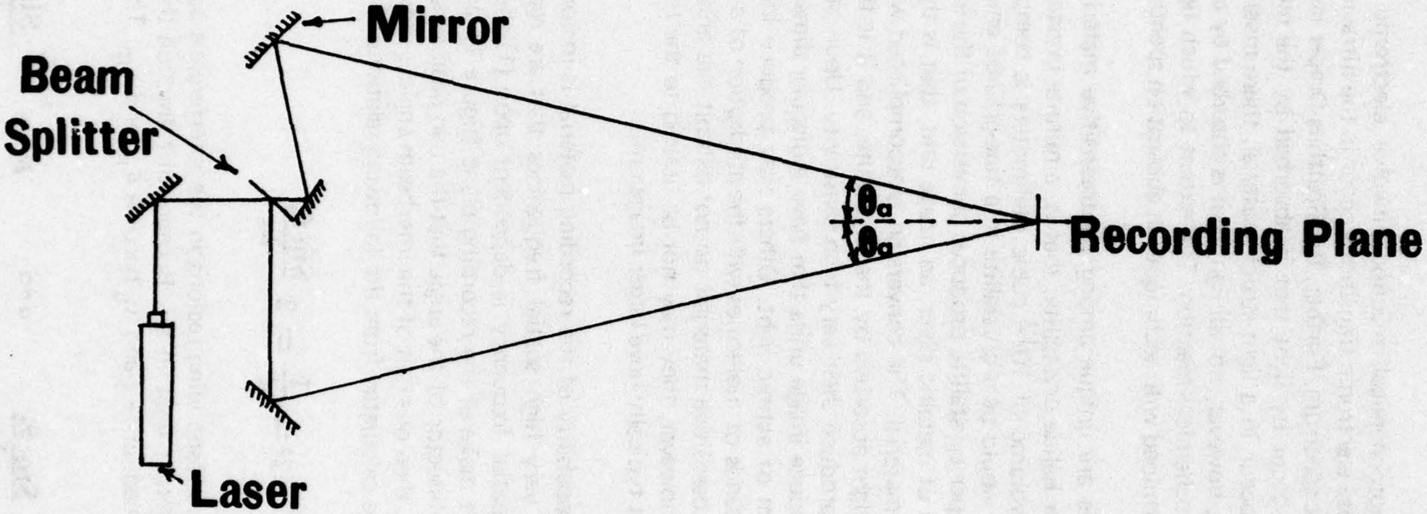


Figure 1. Holographic Optical Arrangements

If $\theta_a$ = 30 degrees and $\lambda_a = 0.633 \times 10^{-3}$ millimeter for the red line of the helium neon laser, then the spatial frequency becomes 1580 lines per millimeters. As $\theta_a$ increases or the wavelength of the coherent light decreases, the resulting spatial frequencies increase. Spatial frequencies approaching 4,000 lines per millimeter have been recorded.

The resolution of images recorded holographically is not the same as the resolution of the recording material needed to record the high spatial frequencies seen in off-axis holography.[8] Factors affecting resolution in images recorded holographically are (1) the dimensions of the hologram (or illuminating beam), (2) resolution of the recording material, and (3) the spatial and temporal coherence of the object illumination. For the case in which the recording material has unlimited resolution and the light is highly coherent so that (2) and (3) are of no concern, the resolution of the image is determined by the dimensions of the hologram (or the illuminating beam). Consider the case for recording a photographic image illustrated in figure 2. The following relationship applies:

$$R_{IMAGE} = \frac{d}{1.22\lambda f}$$

$R_{IMAGE}$ = Resolution of the recorded image
d = diameter of the illuminating beam
$\lambda$ = wavelength of the light source
f = distance from object to hologram recording plane.

Using an F-number (defined by f/d) of five and using $\lambda = 0.633 \times 10^{-3}$ millimeter for the helium neon laser, a resolution of 316 lines per millimeter is obtained for the holographically recorded image.

There are two general categories of holographic storage systems. The more complex and difficult category involves storage of a continuum of information as opposed to discrete information. For example, the holographic storage of photographs consisting of a continuum of density levels requires holographic recording materials with a broad dynamic range. Materials with even a greater dynamic range are needed if storage of many holograms is attempted, as in angular encoding in volume holographic recording materials or if Fourier or near-Fourier transform holograms need to be prepared, even of discrete information such as found on cartographic photographic separations. The dynamic range of the holographic recording material refers to that ability of the recording material to display a broad linear response in density in the reconstructed image to a broad range of exposures used to make the hologram. The storage of discrete information in holographic memory systems is somewhat simpler than storage of

---

[8] B.J. Thompson, "Resolution in Images Formed Holographically - A Summary," Unpublished Tutortial Paper, May 1977.

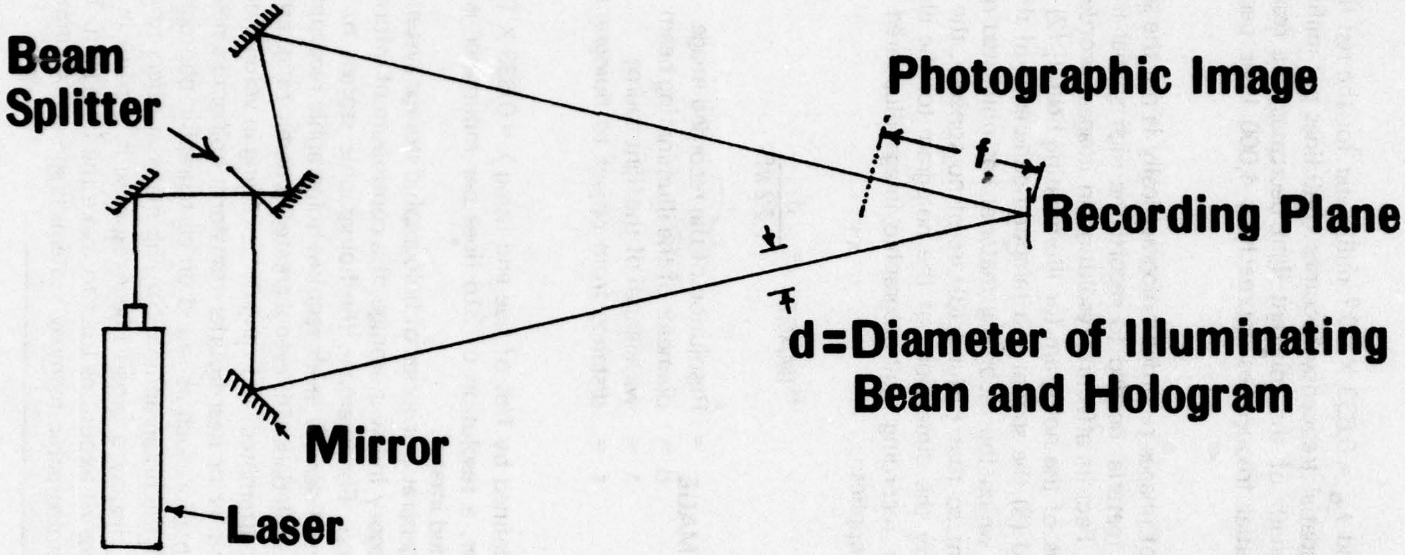


Figure 2. Resolution of Images Recorded Holographically

a continuum of information, except for the recording of Fourier transform holograms which do require recording material with a great dynamic range. Arrangements to store binary bits in an off-axis Fresnel hologram may well exemplify this, and it is the ability of the recording material to record the binary information that is an important measure of performance. This ability, which is the holographic storage capacity of the recording material, can be defined as the square of the resolution of the recorded image. Thus, if the recording resolution is 50 lines per millimeter or 500 lines per centimeter, the holographic storage capacity becomes $(5.0 \times 10^2$ lines per centimeter$)^2$ or $2.5 \times 10^5$ bits per square centimeter. However, the error rate to be expected in interrogating the holographic data bits is dependent upon the contrast ratio. This dependency is treated by Lee.[9] He points out that the storage capacity is determined from knowledge of the error rate and may well be proportional to the reciprocal of the error rate, $P_E$. According to Lee's Table 1, the error rate, and hence the holographic storage capacity in a Fourier transform hologram is dependent upon both the signal-to-noise ratio of the target used and the contrast ratio of the one bit and zero bit in the retrieved signal. This, in turn, is dependent on the contrast ratio in the original data mask. That the signal-to-noise ratio and contrast ratio should be different may not be immediately apparent. Although the contrast ratio is dependent upon the number of one bits in the hologram, the signal-to-noise ratio is not. With an increase in the number of one bits in the hologram, the difference in contrast between the one bit and the zero bit decrease, apparently because of scattering that goes on in the hologram. This difference indicates that any signal-to-noise ratio and contrast ratio studies should include determining the dependency of the measure upon the dimensions of the test target and its design.

## ELECTROSTATIC IMAGING PROCESSES

BACKGROUND (XEROGRAPHY, ELECTROFAX). The dry electrostatic imaging process that is xerography involves preparation of a developed electrostatic latent image on a selenium, or other suitable photoconductive layer, followed by transference of the resulting powdered resinous image to a second substrate by electrostatic means. The powdered resinous image is then fused in a heat zone or through solvent vapors, and the photoconductive layer can be cleaned and re-used many times. The Electrofax process may also be a completely dry process inwhich the electrostatic latent image is prepared on a zinc oxide resin binder layer and subsequently fixed by heat on the same layer. Fine particle pigments prepared in insulating liquids have also been used to produce fixed images on the same layer.

---

[9] Lee Wai-Hon, "Effect of Film-Grain Noise on the Performance of Holographic Memory," *J. of Opt. Soc of Amer.*, Vol. 62, No. 6, June 1972, pp. 797-801.

The sequence of steps involved in the process are electrostatic charging of a clean photoconductive substrate with good surface smoothness, exposing to an image distribution of light to form the electrostatic latent image, developing the electrostatic latent image to form a visible image, and either transferring and fixing the developed image to a second substrate or fixing the image directly to the photoconductive substrate. Several techniques are used to electrostatically charge a photoconductive layer, but the preferred technique involves corona discharge devices. In general, atmospheric corona discharge can be created by impressing electrical potentials greater than approximately 4.5 kilovolts on fine (approximately 50 micrometer thick) wire or needle points. Different electrode configurations, the magnitude of the impressed potentials, and the respective polarities determine the properties of the corona produced. including the amount of ozone generated in the corona (Frank and Buchacek).[10] Exposure of the photoconductive (PC) layer to an image distribution of light is made using a positive transparency. The positive transparency is reproduced as a direct positive image on the layer, and therefore the electrostatic imaging process is a positive-working process that can be made a negative-working process (i.e. a negative film transparency is used to produce a positive image on the PC layer) under special conditions. In a negative-working electrostatic imaging process, the electrostatically produced reproductions exhibit image defects and suffer in image quality to a greater extent than in a positive-working process. The electrostatic latent image formed is not visible until it is developed with either suitable electroscopic powders or liquid developers. The powder grains are generally 2 to 4 micrometers in diameter, and their size limits the resolution to less than 250 lines per millimeter. Electroscopic powders finer than 2 micrometers tend to produce increased background tinting in the nonimage areas and, *hence, a* loss in contrast in the reproduction.

Cascade development with a two-component developer is practiced with xerography. Here the electroscopic powder or toner is mixed with a glass, or other suitable material carrier bead that may be as much as 50 times larger in diameter. The two-component developer is cascaded over a xerographic plate to develop an electrostatic latent image.

Magnetic brush development is also accomplished with a two-component developer in which the larger carrier particles are iron filings. The iron filing mixture is picked up with a magnet and simply brushed across the electrostatic latent image on the PC layer.

Liquid immersion development is carried out with liquid developers prepared ideally as colloidal dispersions with particle sizes in the submicrometer range. Still, stable suspensions of pigment particles between 2 and approximately 20 micrometers

---

[10] C.W.Frank and R. Buchacek, ***A Study of the Effect of Corona Conditions on Electrostatic Printing Processes,*** **U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, ETL-CR-72-17, AD 755 259, 1972.**

in diameter can be prepared if a protective colloid is added to the suspension. One must be careful when using liquid developer to understand the particle size range being used. Not all liquid developers need be colloidal dispersions.

In transferring the developed image to a suitable substrate as is practiced in xerography, the second substrate is placed in position over the developed image, and a corona discharge unit is made to pass over the back of the substrate. The polarity on the corona wire is the same as used to charge the PC layer initially, and the result of this procedure is the transference of most of the toned image from the PC layer to the second substrate. Separation of that substrate from the PC layer reveals an image that is the mirror image to that on the PC layer. Transference of toned images developed by liquid immersion is not easily accomplished, if it can be done at all in the Electrofax process. Fixing of electroscopic powders is accomplished through heating in an oven, in infrared radiation, or with the aid of solvent vapors. In each case, the toner material softens sufficiently to become bonded to the substrate upon solidification. However, such fixing of liquid developers may not be needed. The resinous materials are readily fixed to the substrate. The materials are in a softened state in the dispersing solvent and become hardened with evaporation of the solvent. Under these conditions transference of tone images developed with liquid developers to a second substrate may not be readily done.

Both xerography and the Electrofax process as described above may not be the best processes or the best combination of photoconductors, substrates, and developers for applications in holography. This will be explored in subsequent sections treating electrostatic imaging processes.

PHOTOCONDUCTORS (Se, ZnO, CdS, ORGANIC). Most inorganic photoconductors of interest today are found either in groups IVA and VIA or in combinations of elements from Groups 11B and IVA and Group VIA of the periodic table of the elements. Selenium (Se) alloys, zinc oxide (ZnO), and cadmium sulfide (CdS) consist of elements prepared from these groups. Good review articles that treat these materials in detail include the National Academy of Sciences report[11] and the Dearnaley et al. review.[12] It is amorphous or vitreous selenium containing either arsenic or tellurium that will be referred to as selenium alloy. The presence of these elements modify selenium layers so as either to stabilize the layer to devitrification or to enhance the photosensitivity. The selenium photoconductive layers are predominately used in xerography. Commercially, the layers are available on aluminum substrates. In

---

[11] **National Academy of Sciences, Report of the AdHoc Committee on the *Fundamentals of Amorphous Semi-Conductors*, (National Materials Advosory Board, National Research Council), 1972, p.62.**

[12] **G. Dearnaley, A.M. Stoneham, and D.V. Morgan, "Electrical Phenomena in Amorphous Oxide Films," *Reports on Progress in Physics*, 1971.**

addition to being photoconductive, this material as well as those of ZnO, CdS, and the organic photoconductors are good insulators in the dark. They will retain electrostatic charges in the dark and exhibit only minute, if any, lateral or bulk diffusion of charge following exposure to an image pattern. Amorphous selenium layers are generally opaque to visible and ultraviolet light and along with zinc oxide and cadmium sulfide thick layers will not permit transmission of image information. The zinc oxide is a white pigment as used in the Electrofax process. The pigment is incorporated in a resin-binder matrix (e.g. the silicone resins) when coated on suitable substrate. Commercially, the zinc oxide layers are available on paper substrates. Laboratory coatings dye-sensitizers (e.g. bromophenol blue, rose bengal dye, and acid-free fluorescein) sensitizes the zinc oxide to light in the visible region. The quantum efficiency of such layers is less than one, that is less than one electron is thought to be introduced into the conduction band for each photon of light absorbed. Spectra describing the dye sensitized zinc oxide are reported by Gladden and Chen.[13] Unlike ZnO, CdS can be doped with copper and chlorine atoms to produce a photoconductive material with quantum efficiency approaching $10^3$, while still maintaining a high dark resistivity. The cadmium sulfide layers can be prepared in a resin-binder matrix, but the highly efficient layers are usually a thermally treated (e.g. sintered) or vacuum deposited layer. The doped cadmium sulfide layers are sensitive across the visible region. Thomsen and Bube[14] describe the spectral characteristics of doped CdS layers in their article. Efforts to dope ZnO pigments to produce more efficient layers have not been as successful as those for CdS.

To find transparent photoconductors more suitable to the production of imagery for use in projection systems, one ordinarily turns to the organic photoconductors although thin films of inorganic photoconductors such as CdS may be useable. The most familiar organic photoconductor is the poly-N-vinylcarbaxole-2, 4, 7-trinitro-9-fluorenone charge transfer complex developed by IBM.[15] The poly-N-vinylcarbaxole is sensitized with 2, 4, 7-trinitro-9-fluorenone, and as will be shown later, this charge transfer complex material is the major component in photoplastic film. Epping's

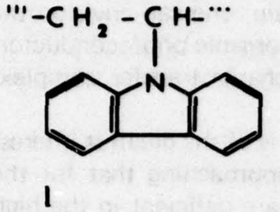
---

[13] James W. Gladden and Pi-Fuay Chen, *Investigation of Continuous Photoconductive Layer Arrays,* U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, ETL-0011, AD A010 642, May 1975, pp. 25-31.

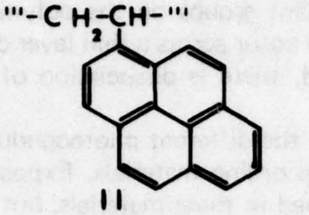
[14] Milton S. Thomsen and Richard H. Bube, "High-Sensitivity Photoconductor Layers," *Rev. of Scientific Instruments,* Vol. 26, No. 7 July 1955.

[15] National Academy of Sciences, Report of the AdHoc Committee on the *Fundamentals of Amorphous Semiconductors,* (National Materials Advisory Board, National Research Council) 1972 p. 64.

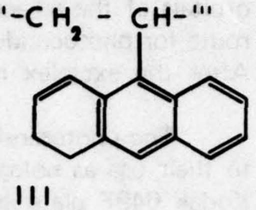
doctoral dissertation[16] addresses poly-N-vinylcarbaxole in detail, and Okamoto[17] et al. discussed organic photoconductors that like poly-N-vinylcarbazole have large pendant pi-electron systems described below as II through VIII. Compound I denotes poly-N-vinylcarbazole that



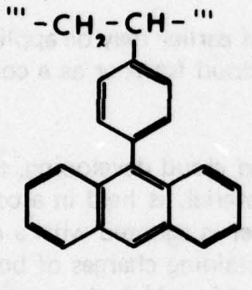
I



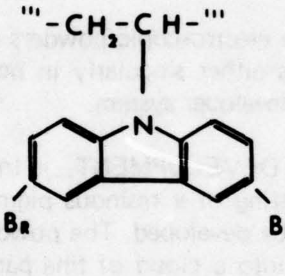
II



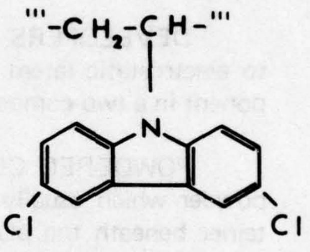
III



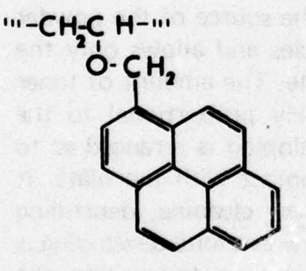
IV



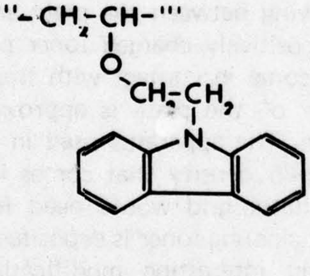
V



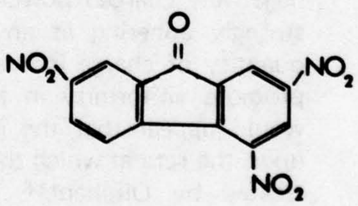
VI



VII



VIII



IX

---

[16] Reinhold H. Epping, ***About the Dependence of the Photoconduction on the Molecular Weight of Poly-N-Vinylcarbazole,*** **University of Munich, 1970.**

[17] **K. Okamoto, S. Kusabayashi, M. Yokoyama, and H. Mikawa, "Current Research on Organic Photoconductors for Electrophotography,"** ***2d International Conference on Electrophotography,*** **Washington, D.C., 24-27 October, 1973.**

complexes with 2, 4, 7-trinitro-9-fluorenone (IX) upon excitation of (IX) with actinic light. Formation of the exciplex (exciplexes are excited complexes composed of an excited *molecule (e.g. IX) that has reacted* with a molecule of a different compound (e.g. I)) permits transfer of an electron to (IX), and with overlapping of the pi-electron orbitals of the adjacent pendant groups on the polymer chain, one can envision the route for photoconduction to occur across a thin layer of the organic photoconductor. After the exciplex is formed, there is dissociation of the charge transfer complex.

The photosensitivity of the different photoconductors is of the greatest interest to their use as holographic recording materials. Exposures approaching that for the Kodak 649F plate are observed in these materials, but they are deficient in the high resolution and diffraction efficiency associated with more conventional holographic recording materials. Perhaps reconsidering approaches to hologram recording, particularly with the more transparent organic photoconductors, will enhance use of electrostatic imaging processes for this purpose.

DEVELOPERS. The electroscopic powders referenced earlier may be applied to electrostatic latent images either singularly in powdered cloud form or as a component in a two-component developer system.

POWDERED CLOUD DEVELOPMENT. In powdered cloud developing, the powder which usually consisting of a resinous pigmented material, is held in a container beneath the plate to be developed. The powder or toner is agitated with a rotating *brush and is whirled into a cloud* of fine particles containing charges of both polarity. The degree of charging is independent of the method in which the powder is agitated. If negatively charged particles are to be deposited on the plate, a negative potential is impressed on a grid of wires (precipitator grid) placed in close proximity to the xerographic plate and lying between the plate and the source of the powder cloud. This wire attracts the positively charged toner particles and allows only the negatively charged powder to come in contact with the plate. The amount of toner strongly adhering at any area of the plate is approximately proportional to the quantity of charge in that area. The apparatus used in developing is arranged so to promote uniformity in the cloud density that comes in contact with the plate. It would appear that the precipitator grid would need frequent cleaning, depending upon the rate at which the participating toner is deposited. Powder cloud developing is treated by Oliphant[18] and an interesting modification using a two-component developer is given by Walkup.[19]

MAGNETIC BRUSH DEVELOPMENT. In magnetic brush developing the pigmented resinous material or toner consists of particles approximately 2 micrometers

---

[18] **W.D. Oliphant, "Xerography: A Non-Chemical Photographic Process,"** ***Discovery*****, Vol. 14, 1963, p. 175.**

[19] **Lewis E. Walkup, "Method for Developing Electrostatic Images," U.S. Patent 2,784,109.**

in size. The toner is thoroughly mixed with iron filings that are approximately 50 to 100 micrometers in size, and the mixture is picked up with the aid of a magnet. Upon contact between the toner and the iron filings, the toner will become charged and the iron filings will become charged opposite in polarity to that of the toner. The mechanism that produces a charge transfer between two dissimilar materials after contact is made, is often referred to as the triboelectric effect. For the toner to work in a positive working process, the charge that is produced on the toner material itself must be opposite to the charge that is deposited on the plate by the corona discharge. Then, for the toner to work in a negative working process, the charge that is produced on the toner material by the triboelectric effect must have the same polarity as used to corona charge the PC layer. In this case, the toner particles are repelled by the corona-charged areas and by some mechanism are deposited in the light-struck areas on the plate. Further details of negative working processes that comprise reversal development is treated by Gillespie.[20]

CASCADE DEVELOPMENT. The same mechanisms noted in magnetic brush developing apply to cascade developing. In this type of developing, more specific properties may be built into the carrier particles used instead of the iron filings essential to magnetic brush developing. In a positive working process, the carrier particle, whose size is between 30 and 60 mesh, must acquire the same charge when placed in contact with the toner particles as the charge deposited on the PC layer by the corona discharge. The carrier particles must have a lesser attraction for the toner than the respective charged areas on the PC layer. The ratio by weight of toner to carrier particles lies between 1:15 to 1:100. Walkup and Wise describe this type of two component developer in their patent.[21]

LIQUID IMMERSION DEVELOPMENT. Perhaps the most promising method of developing electrostatic images for applications as holographic recording materials is liquid immersion development. As previously stated, liquid developers can be prepared as colloidal dispersions in which particle sizes are below 2 micrometers. By barring any inhomogeneities in the PC layer, holographic imagery may be produced with resolutions in excess of 1000 lines/mm. Particle sizes below 0.5 micrometers are estimated to have this capability. Resolutions of 128 to 144 lines/mm are readily obtained in the laboratory. These resolutions are determined using the U.S. Air Force resolution target placed in contact with the charged PC layer under glass, but without a vacuum printing frame being used.

In preparing the liquid developers, it is important to select a solvent that does not disrupt the PC layer. It is possible that the zinc oxide-resin binder layers and the

---

[20] H.C. Gillespie, "Magnetic Brush Reversal Powder Development on Zinc Oxide-Binder Layers," *2d Symposium on Unconventional Photographic Systems,* Washington, D.C., 26-28 October, 1967.

[21] Lewis E. Walkup, and Edward N. Wise, "Developer Composition for Developing an Electrostatic Latent Image," U.S. Patent 2,638,416 - assigned to Battele Development Corp.

organic photoconductor layers will dissolve in the developer solvent. Hence, attention must be given to the liquid developer-photoconductive layer compatibility. Methods for preparing liquid developers will be found described by Fauser and Walecka[22] and also by Klein.[23] These methods use kerosene type solvents (e.g. Isopar G) that have low sulfur content, have a high electrical resistivity, and have been found compatible with certain zinc oxide-binder resin layers. The resin used in the liquid developer is soluble in the high resistivity solvent, forming an organosol and protective colloid for the pigment particles also dispersed therein. Fauser used Rohm and Haas long oil, alkyd Duraplex D65A. The resulting polarity of the charge on the pigment particles is independent of this alkyd resin for a series of different carbon blacks and copper phthalocyanine blue and green pigments dispersed in the high resistivity liquid either with or without the resin. In experiments at ETL, the impingement blacks and the phthalocyanine green pigments developed a negative charge on their pigments when dispersed in the high resistivity liquid, and the furnace blacks and the copper phthalocyanine blue developed a positive charge. It is interesting to note that the negatively charged pigment particles are also the particles that are known to have electron withdrawing or electronegative elements on their surfaces. The impingement carbon blacks have a carbonoxy complex on their surfaces, and the copper phthalocyanine green pigments are formed by chlorinating copper phthalocyanine blue. In the case of liquid developers then, perhaps triboelectric charging of the different pigments is masked by intraparticle charge transfer with formation of dipole.

One aspect of electrostatic printing processes leads to loss of contrast in imagery containing large areas, particularly solid areas. This aspect is associated with orientation of electrostatic fields of force that is nearly normal or perpendicular to the image plane at the edges and to within 6 millimeters of the edges. Beyond this 6 millimeter region the electrostatic field lines of force become more horizontally oriented to the surface of the image plane. In this condition, very little toner or imaging material is deposited in the affected area. With the introduction of a counter electrode near the surface of the electrostatic latent image, the electrostatic lines of force can all be made normal to the image plane and good coverage of the large image area is obtained. The spacing of the counterelectrode from the surface of the image plane is approximately 1.5 millimeters or less. Hence, using liquid developers rather than electroscopic powder developers facilitates somewhat using counterelectrodes, although using counterelectrodes with dry developers is known and, of course, the magnetic brush development method has a built-in counterelectrode. With consideration being given to the fine particle size with which liquid developers may be prepared and the ease with which counterelectrodes may be designed and fabricated for use with liquid developers, one then may predict that liquid developers should prove to be more successfully developed for

---

[22] D.L. Fauser and J.A. Walecka, *Development of Image Forming Materials,* U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060. NTIS AD-430-090L.

[23] Otto C. Klein, *Research in Continuous Tone Electrophotography,* U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, December 1962, NTIS AD-101-863, p.65.

holographic purposes.

SCOTT GRAPHIC TEP FILM. The TEP film is an amplitude recording material that uses an organic photoconductor in contact with a conductive polyester film. The photoconductive material consists of a crystalline m-phenylene diamine derivative dispersed in a polymer matrix with spectral sensitizing dyes. Like the poly-N-vinylcarbazole layers, this material is transparent. The imaging material consists of carbon black pigment particles in a suitable polymer system with a high resistivity liquid. The toner particles are 0.6 micrometer in diameter. A two-component dry developer has been used, but there is no information on the toner particle size.

Zech[24] has examined the holographic properties of the Scott Graphics TEP film designated XP5-004. This particular film was selected from a few different types of TEP film and liquid developer following preliminary tests. The information storage is accomplished on a positively charged photoconductive film by applying a positively charged toner material in a high resistivity liquid. Hence, the process is negative working. It can be made positive working, however, through adjustments of polarity either on the photoconductive film or on the developer toner particles.

The information storage process consists of corona charging the Scott Graphics TEP film followed by exposing the charged layer to an image (exposure sensitivity at 632.8 nanometers is approximately 0.25 millijoules per square centimeter) and developing with either a dry or wet developer. The image may then be fixed by using heat or by air drying. Fixing the image tends to reduce the optical density of the finished image. It is interesting to note that in addition to the image consisting of spatial variations in absorption (optical density) there are also surface relief effects observed by Zech. Thus, for holographic recordings, the TEP film also exhibits some planar phase characteristics.

ORGANIC PHTOTCONDUCTOR WITH A 10 TO 100 NANOMETER.
ORGANOSOL DEVELOPER. The prospect of using a transparent polymer developer to produce a phase surface hologram on a transparent organic photoconductor or even a transparent inorganic photoconductor (e.g. evaporated CdS layer) is explored here, although such has not been reported in the literature. The choice of an organosol type developer suggests itself because some organosols are known to form stable colloid dispersions to aggregation and have sufficiently high electrical resistivity so as not to disrupt the electrostatic latent image. The term organosol is used to denote colloids that are dispersed in an organic solvent. There are many natural and synthetic high molecular weight polymers, such as rubber, polystyrene, the alkyd resins, and polymethyl methacrylate that dissolve in appropriate organic solvents to form stable organosols. It is important to know something about the shape as well as the size or

---

[24] **Richard G. Zech, *Holographic Recording Materials*, Final Technical Report F30602-74-C-0030, Rome Air Development Center, Griffiss AFB, New York, July 1974.**

molecular weight of the sol. Many high molecular weight polymers such as polyethylene, rubber, and possibly the long-chained alkyd resins are thread or filament shaped. These may form sols that would be nondiscriminating in any deposition on electrostatic charged latent images. Polymers that form stable organosols with either spherical or ellipsoidal shape and with a definite surface charge are needed. Since the polymer must develop a surface charge of a single polarity, the dispersing solvent should exhibit a degree of polarity and must exhibit an appropriate electrical resistivity. Surfactants may be added to adjust the surface charge on the sol and increase stability of the dispersion.

Streifer and Stark[25] consider the theoretical aspects of developing an arbitrary one-dimensional periodic charge pattern with a high charge density toner of a dimension that is small compared to the periodic image pattern. The transfer function for the developed xerographic image is a function of the dielectric constant of the photoconductive layer, the toner material, and the magnitude of the uniform surface charge of the toner. The spatial frequency at which the modulation transfer is $(2)^{-1/2}$ is found to increase with increases in toner charge density and decreases in the surface charge on the photoconductive layer. Eastes et al.[26] have determined the number of electrons per toner particle and found them to be approximately 500 electrons per particle for pigment organosols dispersed in an isoparaffin solvent. The average toner particle sizes determined using microscopy at 1500 diameters were approximately 0.5 to 0.8 micrometer with less than 5 percent in the 1- to 2-micrometer range. It may be possible to find stable polymeric colloidal materials in the 10 to 100-nanometer-diameter range with sufficiently high charge density. Also, care is needed to select the organic solvent with a sufficiently high resistivity (approaching $10^{15}$ ohm-centimeter) but with a suitable degree of polarity[27] to stabilize the needed charge density for the polymeric sol. The corona charging devices capable of producing a uniform surface charge on the photoconductive surfaces have been described by Albrecht and Epping.[28] Using a high frequency potential impressed on a constant dc-potential in the corona unit produces the needed uniform surface charge. This description does not resolve all problems with recording surface phase holograms with electrostatic imaging materials, but it is set forth here as an effort to show how one may be able to work out a method or record such holograms in a more promising non-silver photosensitive material.

---

[25] **W.M. Streifer and Howard Stark, "Some Theoretical Aspects of High Resolution Xerographic Development," *Applied Optics*, Supplement 3: Electrophotography, 1969, pp. 149-153.**

[26] **J.W. Eastes, H.C. Gillespie, and H. Wielicki, "Draft Specifications for Multicolor Electrostatic Printing Materials," *TAPPI*, Vol. 52, No. 5, May 1969, pp. 872-6.**

[27] **H.C. Gillespie, W.M. Lee, and G. Lozier, *Continuous-Tone Electrophotography*, U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, August 1968, NTIS AD-673-881, p.17.**

[28] **J. Albrecht and R.H. Epping, *Investigations on the Transfer of Full-Tone Reproduction in Electrophotography*, Translation No. T-1929-68, U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, 1968, NTIS AD-837-289.**

PHOTOPLASTIC FILM OR THERMOPLASTIC XEROGRAPHY (KALLE). About 1962 phase surface holograms were prepared on so-called photoplastic layers that were initially developed for the frost deformation process. In the frost deformation process a photoconductor, such as the aforementioned organic photoconductor, polyvinylcarbazole, sensitized with 2, 4, 7-trinitro-9-fluorenone is coated on a transparent conducting substrate that has been deposited on a suitable substrate (e.g. glass or Cronar film). The conducting layer usually consists of doped tin or indium oxides, evaporated gold, gold-chromium alloy, or silver. Another thermoplastic layer, Staybelite Ester 10, a natural tree resin, or polystyrene, is deposited on top of the photoconductive layer. In the frost deformation process, the photoplastic layer is arranged in a corona discharge assembly and given a uniform electrostatic charge. Exposure of the charged layer may not discharge the electrostatic charge on the air interface surface of the thermoplastic layer but does promote transference of charge across the photoconductive layer to the photoconductor-thermoplastic layer interface. Recharging of the photoplastic layer with a corona discharge adds charge to the surface of the thermoplastic layer in the exposed regions. The photoplastic layer is then heated to the softening temperature of the thermoplastic layer (generally 50° to 100° C). The electrostatic forces deform the surface of the thermoplastic layer until the forces are balanced by the surface tension of the material. Cooling the surface of the photoplastic fixes the quasi-random frosted pattern of the image. The scattering afforded by the frosted image is readily defined upon projection. These areas would appear darker than the regions of the thermoplastic not deformed by the process. Reheating the thermoplastic layer containing the frosted image to a higher temperature than used to produce the deformation of the layer tends to restore the photoplastic film to its original state. Thus, the material has a write-erase capability.

Holographic recordings on the photoplastic materials have been studied by Credelle and Spong[29] of RCA and Goetz et al.[30] of Bendix Research Laboratories. They describe the unique response of the thermoplastic layer to spatial frequencies that is dependent upon the thickness of that layer. The corrugation pattern formed in the thermoplastic surface replaces the quasi-random, frosted pattern in large part. The bandwidth of the spatial frequency response has been empirically determined and found to be about (1/6 T) in which T is the thickness of the thermoplastic layer. Goetz et al. succeeded in increasing the bandwidth by means other than decreasing the thermoplastic layer thickness. The selection of a thermoplastic (e.g. low-molecular-weight polystyrene) with low conductivity at flow temperatures produced bandwidths three times that predicted by the empirical formula. Since the increased bandwidths produced improvement in the low frequency response of the photoplastic film needed for Bendix's application, RCA used the narrower bandpass spatial frequency response

---

[29] T.L. Credelle and F.W. Spong, "Thermoplastic Media for Holographic Recording," *RCA Review*, Vol. 33, March 1972, pp. 206-227.

[30] G. Goetz, R.K. Mueller, and D.M. Shupe, "Recent Progress in a Real-Time 3-D Display," *Proceedings of IEEE Conference on Display Devices*, New York, October 1972.

to reduce intermodulation distortion and achieve undistorted high efficiency reconstruction. The technique reduces the effects of substrate reflections and of other spurious and weak sources. Credelle and Spong's article describes two variations in the process sequence of corona charge, expose, recharge, and heat developing. In the first of these, the phototplastic layer is heated and then corona charged and exposed simultaneously. This simultaneous recording produces virtually frost-free, highly efficient, high resolution holograms. First order diffraction efficiencies that exceed the theoretical diffraction efficiency for sinusoidal thin phase gratings of 34 percent have been obtained. A blaze effect is observed upon tilting the gratings from normal incidence such that up to 60 percent of the transmitted light is diffracted into the first order. In the second variation, the usual sequence in processing the photoplastic image is followed by a post development step in which the hologram is recharged and reheated either simultaneously or sequentially. As a result the surface grating is deeper, thus increasing the diffraction efficiency. The post development process may be repeated several times and is limited only by an increase in frost noise. Finally, since the hologram recording is a surface relief process, the hologram can be used as a master in self replication by embossing techniques in use at RCA. More about RCA's embossing methods will be found in the section on PHOTORESISTS.

The photoplastic films or plates have photosensitivities approaching the Kodak 649F spectroscopic plate. With the capability of 1,000 millimeters$^{-1}$, the photoplastic imaging process demonstrates the most promising of the electrostatic imaging process for holographic recording. It could well be among the more promising non-silver imaging processes as well.

GALVANIC CELL ELECTROPHOTOGRAPHY. H. Kokado[31] of the Tokyo Institute of Technology described a galvanic cell type electrophotography in which an exposed zinc oxide resin layer on an aluminum substrate forms a galvanic cell in a developing solution of nickel chloride or 2, 3, 5-triphenyltetrazolium chloride (TTC). The light struck zinc oxide resin layer retains a memory of the amount of light incident on the layer as the result of the photodesorption of oxygen from the surface of the zinc oxide crystallites described by Heiland et al.[32] The following series of equations suggest themselves and may describe the chemistry involved.

$$\mathrm{ZnO} \xrightarrow{\text{light}} \mathrm{Zn^{o}} + \tfrac{1}{2}\mathrm{O_2}$$

**Memory Effect that persists until atmospheric oxygen chemically reacts with the** $\mathrm{Zn^{o}}$**, or the following occurs,**

$$\mathrm{Zn^{o}} \rightarrow \mathrm{Zn^{++}} + 2e^{-} \quad \text{Oxidation (Anode)}$$

$$\mathrm{Ni^{++}} + 2e^{-} \rightarrow \mathrm{Ni^{o}} \quad \text{Reduction (Cathode)}$$

$$\mathrm{ZnO} + \mathrm{Ni^{++}} \rightarrow \mathrm{Ni^{o}} + \mathrm{Zn^{++}} + \tfrac{1}{2}\mathrm{O_2} \quad \text{Net Cell Reaction}$$

---

[31] H. Kokado, Y. Ohba, and E. Inoue, "Galvonic Cell Type Electrophotography Utilizing Photoconductive Memory of ZnO-Resin Layers," *Fourth Society of Photographic Scientists and Engineers Conference on Unconventional Photographic Systems,* Arlington, Va., 21 November 1975.

[32] G. Heiland, E. Mollwo, and F. Stockmann, "Electronic Processes in Zinc Oxide," *Solid State Physics,* Vol. 8, Academic Press, 1959, pp. 278-295.

Since the anode potential $E^o$ (Anode) is - 0.763 and the cathode potential $E^o$ (Cathode) is - 0.250, the overall cell potential is $E^o$ (Cathode)- $E^o$ (Anode) = +0.513, in which the positive value denotes the cell reaction described above is spontaneous. Thus, we do have a galvanic cell. The cathodic reduction of nickel chloride produces black nickel metal and of TTC gives a red formazan-water-insoluble pigment. The reduction occurs in the light struck regions and is proportional to the log of the exposure, as described by Kakado, over at least one decade. Thus, image-wise deposition of either nickel or formazan occurs. No information on image resolution was given, but the cathodic reduction of nickel and formazan should give rise to image materials in the below-micrometer range. The method may have applications in hologram storage, although the imagery may have to be opaque in character. Finding of a transparent photoconductive material with a useful memory effect would be helpful.

## PHOTORESISTS

BACKGROUND. Resists have been used in the intaglio printing process since the early 16th century, although the technique of etching did not fully mature until the following century. Using acid resists on metal plates enabled the artists to use acid solutions, or mordants, to etch lines into the plate that correspond to the scribed lines in the resist material. These early acid resists known as hard grounds, consisted mainly of wax but also contained modifying ingredients, such as asphaltum, amber, mastic, and tallow. Liquid grounds could be prepared by dissolving different hard grounds in ether or chloroform. Adding petroleum jelly, grease, or fat to the hard ground produces a soft ground that does not harden in its resist form. Powdered resins such as gilsonite dusted on the surface of a metal plate and heat fused are used to produce tonal variation in intaglio prints. The technique is called aquatint. Each resin particle melt becomes an acid-resistant dot around which the mordant produces a cavity that deepens with time in the etching process. Development of the acid-resists and the etching process was a technical breakthrough of the 16th and 17th centuries that started commercial reproductions of prints.

From the foregoing, we see that the resist material has the primary function of forming an acid-resistant layer to protect a metal plate from mordant attack. Modern day resists contain light-sensitive compounds that produce a solvency differential between the unexposed and exposed regions. These photoresists have additional utility in forming electrical resists for use in metal plating and ion milling, and alkali resists as well as acid resists for chemical etching. Development of the light-exposed photoresist with suitable solvents promotes dissolution of either the unexposed or the exposed regions, depending upon whether the resist is negative or positive working respectively. Although the photoresists used in holographic recording today have the ability to resist electrical conduction or chemical attack, these attributes are not essential to the utility of the hologram. The recording of the holographic interference pattern in relief or a surface variation is essential, however, and enabling preparation of a reflection hologram through evaporative metal processes and multiple duplication of holograms via embossing techniques. these techniques will be described in more detail later.

The earlier photoresists were developed for use in intaglio or so-called deep etch printing process. Here, unhardened dichromated gelatin was used as the more important photoresist material prior to the development of newer photoresist materials, consisting of the photopolymers, the diazo, the diazo-oxides, and the azides. There are other classes of materials that may be used as photoresists, but they are not used as much. The photopolymers will be discussed in a separate section as a phase volume material. In addition, the diazo, diazo-oxides, and azides may also be used as a phase volume material, particularly when coupled with suitable coupling compounds. The dichromated gelatin has characteristics of one of the more efficient holographic phase materials but a very short shelf life prohibits its commercialization. The appearance of the diazo, diazo-oxide, and azide materials in plate coatings for planographic printing and as photoresists for intaglio printing marked the commercialization of presensitized printing plates and the decline of the dichromated gelatin and other colloidal protein dispersions. It appears then that the diazo, diazo-oxide, and azide materials should find their way into the commercially available holographic recording materials, and we will see later that perhaps the first of these is the Shipley positive photoresist.

## DIAZOS, DIAZO-OXIDES, AND AZIDES

CHEMICAL PREPARATION OF THE DIAZO COMPOUNDS. The diazo compounds were first announced by Johann Peter Griess in 1858. The compounds were prepared by treating an alcoholic solution of picramic acid (i.e. 2-amino-4, 6-dinitrophenol) with dinitrogen trioxide that is the anhydride of nitrous acid. In 1866 a collaborator of Griess, Carl A. Martius[33], first prepared diazo-aminobenzene using sodium nitrite in the aqueous solutions of aniline salts. In 1970, Schelly[34] described diazotization as the nitrogen (N)-nitrosation of primary aromatic amines promoted by an electrophilic substitution of the nitrosyl ion for the two amino hydrogens. The nitrosyl ion may be furnished as such or bound to a Bronsted base (e.g. $NO^+$ which is the nitrosyl ion; $NO \cdot OH_2^+$; $NO \cdot X$; $NO \cdot NO_3$, $NO \cdot NO_2$, which is the dinitrogen trioxide used by Griess; and $NO \cdot OH$). The overall diazotization reaction is formulated as follows:

$$\text{Aromatic Amine, } ARNH_2 + 3HX + NaNO_2 \xrightarrow[\text{excess HX}]{0\text{-}5^\circ C} (ARN_2^+)X + NaX + 2H_2O + HX$$

**The excess acid is needed to prevent formation of diazotates from diazonium ion, $ARN_2^+$.**

---

[33] David H. Wilcox, "History of the Use of Sodium Nitrite in the Diazotization Reaction," *American Dyestuff Reporter*, 24 October 1966, pp. 891-3.

[34] Zoltan A. Schelly, "Effect of the Solvent on the Kinetics of Diazotization, " Air Force Office of Scientific Research, Arlington, Va., January 1970, AD-721-766.

Schelly's description of diazotization is further explained by the following mechanism of the diazotization reaction. There is an electrophilic attack by the nitrosating agent (the first five species in the preceeding list in acidified water or by NO·OH prepared in methanol) on the lone pair of electrons on the primary amine followed by a rapid sequence of steps leading to the formation of the diazonium ion, as follows:

$$ARNH_2 + NO^+ \xrightarrow{\text{slow}} ARNH_2 \cdot NO^+ \text{ (This is the rate determining step.)}$$

$$ARNH_2 \cdot NO^+ \longrightarrow AR{\cdot}NH{\cdot}NO + H^+$$

$$AR{\cdot}N{:}N{\cdot}OH$$

$$(AR{\cdot}N{:}N)^+ + OH^-$$

Schelly learned that in methanol, carbon tetrachloride rather than water reaction solutions, the diazotization reaction rate increases and the activation energy decreases. This supports the contention that diazotization proceeds as an electrophilic attack on the base and not on the anilinium ion, which is also formed in acidified aquous solutions. Zollinger[35] describes this and states that there is an equilibrium between the base and the anilinium ion that is important to the process. Thus,

$$\text{(Promotes reaction) } ARNH_2 \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} ARNH_3^+ \text{ (Promotes solubility of the amine)}$$

The nitrosating agents and the dissolution of aromatic amines in aquous solutions are favored by increasing the hydrogen ion concentration, but the increased acidity is in conflict to more favored basic aromatic amine needed for the diazotization reaction. Thus, the diazotization reaction then favors the weaker basic amines.

Diazotization of amines with alkali nitrites (e.g. sodium nitrite) is a quantitative reaction. Diazotization is carried out by adding the acidified nitrite solution to the acidified amine solution such that the nitrite is not added in excess of $10^{-4}$ mole per liter; any excess would be detrimental. Standard solutions of sodium nitrite are used, and the concentration of the diazotizable amine is actually determined through titration to a blue color with starch, potassium iodide paper. It is the acid nitrite in slight excess that produces the color change. Usually 2.5 moles of mineral acid are used per mole of amine, and an equivalent mole of nitrite is used per mole of amine. Ice made from distilled water is added directly to the reaction mixture to insure the reaction temperature does not exceed 5°C. Practice is needed in carrying out successful diazotizations.

The high degree of solubility of diazonium salts in water makes their isolation from this medium difficult. Thus, to obtain pure, solid salts, diazotization has been carried out in alcohol, acetic acid, dioxane, and other media using esters of nitrous acid

---

[35] Heinrich Zollinger, Harry E. Nursten, Ed. and Trans., *Azo and Diazo Chemistry Aliphatic and Aromatic Compounds,* Interscience Publishers, New York, 1961.

or alkylinitrites. Dilution with ether produces isolation of pure diazo compounds from the alcoholic solutions. In the interest of reducing the instances of explosions however, the diazo compounds are dried carefully and only in small quantities. Stabilized diazonium salts that are commercially available contain only 20 to 25 percent by weight of the salt and 75 to 80 percent of the stabilizers and diluents. An alternate method used to obtain stabilized diazo compounds from aquous solutions is that of adding complexing salts to the diazotization solution and precipitating the diazo compounds as complex salts. Nuttall et al.[36] describe a series of diazonium chloride· chlorometallates or double salts prepared following diazotization of the corresponding amine hydrochloride in 50 percent hydrochloric acid solution with the appropriate quantity of sodium nitrite by precipitating the double salt in solutions of the metal chloride in dilute hydrochloric acid. For example, the fluoroborates were precipitated upon addition of the diazo compounds to 40 percent aqueous fluoroboric acid, and the hexafluorophosphates were precipitated from an aqueous solution of potassium hexafluorophosphate. The diazonium chlorides include those of benzene, meta-toluene, ortho-and para-toluenes, O-, M-, and p-nitrobenzene, 0- and m-trifluoromethylbenzene, and p-aminobenzene. The double salts prepared included not only fluoroborate, $BF_4^-$, and hexafluorophosphate, $PF_6^-$, but also $HgCl_4^{-2}$, $ZnCl_4^{-2}$, $CdCl_4^{-2}$, $SnCl_6^{-2}$, $Fe(CN)_6^{-3}$, and $FeCl_4^-$. It is interesting to note that the shifts in the characteristic band, between 2100 and 2300 cm$^{-1}$, that are assigned to the stretching frequency of N-N, are associated with the different cations such as $BF_4^-$ and $PF_6^-$. A shift to lower frequencies or longer wavelengths is attributed to partial covalent bonding. The compounds containing $BF_4^-$ and $PF_6^-$ exhibit the more ionic type bonding with the diazo group. Further, the spectral sensitivity may be related to the degree of ionic character of this bonding. Thus, formation of the double salts of the diazo compounds leads to compounds with greater chemical stability that are readily isolated and that may be adjusted with respect to their spectral sensitivity to some extent.

DIAZO RESIN. The appearance of the diazo resin, namely the formaldehyde condensation products of p-diazodiphenylamine, is of significant importance to the diazo story to warrant discussion here. Early treatment of the diazo resin was made by Jewett and Case.[37] Although the patent treats the preparation of aluminum plates to receive the diazo resin, it also describes a preparation for the zinc chloride double salt of the diazo resin. The sulfate salt of p-diazodiphenylamine was first obtained from the Fairmount Chemical Co., Inc., Newark, N.J., although it is available from other sources today (such as Chemicals Procurement Laboratories, Inc., College Point, N.Y.). The procedure is carried out under yellow safe light conditions. Briefly, 34 parts by weight of the p-diazodiphenylamine sulfate is mixed with 3.25 parts of paraformaldehyde, 4.5 parts anhydrous zinc chloride and introduced into 135 parts of cool ($<6^{\circ}C$) $66^{\circ}$ Baume sulfuric acid. The brown solution is slowly poured on twice its weight of ice to produce a black tarry material. The tarry material is dissolved in water. The addition of

---

[36] R.H. Nuttall, "The Infra-Red Spectra of Some Stable Diazonium Salts," *Spectochimica Acta,* Vol. 17, 1964 pp. 947-952.

[37] C.L. Jewett and J.M. Case, "Planographic Printing Plate," U.S. Patent 2,714,066, 26 July 1955.

any excess, saturated zinc chloride solution precipitates a yellow solid, which is filtered off. The solid is purified by reprecipitating from water by adding an alcohol. A 1 percent solution of the purified diazo resin is applied to suitable substrates for printing purposes. Other preparations for this important condensate will be found in the extensive patent literature.[38, 39, 40]

The UV-VIS spectra of the p-diazodiphenylamine sulfate and the diazo resin show that the sulfate has a broad peak with a maximum absorption at 377.5 nanometers that extends well above 400 nanometers into the visible region, and the resin has a broad peak with a maximum absorption at 371.0 nanometers that also extends well above 400 nanometers into the visible region. The spectra and diazo resin were prepared in-house, and water solutions were used to obtain the spectra of the respective photosensitive materials. Irradiation of aqueous solutions and perhaps dry layers of either the diazo compounds or the diazo resin with light in the respective absorption bands may produce a free radical specie of the form proposed by Zandstra and Evleth.[41] Such radicals are known to promote photocrosslinking in a similar manner to the dichromates. To this extent, the diazo compounds and possibly the diazo resin may be used to sensitize gelatin and other monomer and polymer compounds to form photosensitive layers with good spectral sensitivity in the blue and the near ultraviolet region namely 340 to 450 nanometers. This will be amplified next.

DIAZO SENSITIZED LAYERS. The literature contains a number of patents that describe layers formed of compounds or materials such as gelatin that are sensitized with diazo, diazo oxide, and even the azide compounds. However, the difficulties encountered include crystallization of the sensitizing compounds in the emulsion, and emulsion defects such as pinholes and other nonuniformities. These difficulties are not always described in the patent literature; but in certain patents they are described. For example, the diazo compounds will precipitate out or form crystalline salts in some layers. Selection of compatible compounds retards or eliminates this and has lead Borchers[42] to disclose in his patent that coatings free from precipitated salts may be prepared from diazonium salts, organic poly-acid, and sufficient hydrochloric acid in solution to prevent precipitation. Examples of diazo salts include diphenylamine -4 diazonium and the corresponding condensation products prepared with formaldehyde. Polyvinylphosphonic acid is an example of the organic poly-acid. The

---

[38] M.P. Smith and R. Zahn, "Diazo Compounds and A Process of Preparing Them," U.S. Patent 2.063,631, 8 December 1936.

[39] J.F. Dowdall and J.M. Case, "Planographic Printing Plate," U.S. Patent 3,136,636, 9 June 1964.

[40] William Neugebauer, H. Stephan, and A. Reben Stock, "Presensitized Foil for Planographic and Offset Printing," U.S. Patent 3,235,382, 15 February 1966.

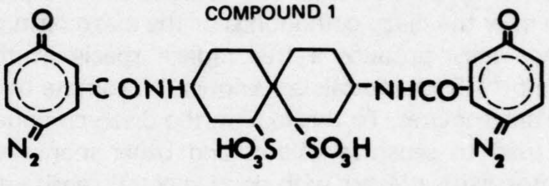
[41] P.J. Zandstra and E.M. Evleth, "Photolytic Decomposition of Aryldiazonium Salts. The p-Dimethylaminophenoxy Radical," *J. Amer. Chem. Society,* Vol. 86, 1964 pp. 2664-2666.

[42] Henning H. Borchers, Hartmut Steppan, and Fritz Uhlig, "Process For the Preparation of A Printing Plate Presensitized with A Diazonium Salt," U.S. Patent 3,510,307, 5 May 1970.

coating has excellent stability in layers on aluminum plates without precoats and should exhibit good stability on glass and polyester film if the sensitizing solution wets these substrates uniformly producing layers without the aforementioned defects. Schmidt and Süs[43] describe diazoquinone compounds with the general formula $R{-}CO{-}NH{-}R_2NH{-}CO{-}R_1$ that may be used to sensitize a number of different colloidal materials. Here R and $R_1$ are quinone - (1, 4) - diazide radicals, and $R_2$ is an arylene radical having at least one $-SO_3H$ group. The colloidal materials include gelatin, casein, highly viscous polyvinyl pyrrolidones, acrylic acid amides, polyvinyl alcohol, or similar water-soluble or water-swollen colloids.

**A chemical preparation is described in the patent for the synthesis of the compound**

COMPOUND 1



**Substrates that are reported to be coatable by dispersions of the sensitized colloids include paper, films, plastic foils, metal foils, metal plates and cylinders of aluminum, zinc, copper or brass, glass, and textile fabrics.**

Compound I in the amount of 0.15 gram is suspended in 85 $cm^3$ (cubic centimeters of 50 percent aqueous alcohol solution and dissolved by neutralizing the acid component with sodium bicarbonate solution. The resulting solution is added to 15 $cm^3$ of a 10 percent aqueous solution of highly viscous polyvinyl pyrrolidone and filtered. This solution is then used to coat an aluminum plate. After exposure, the plate is developed with water. Still, another patent by Mainthia[44] treats sensitized polyurethane resins. The polyurethanes include the Estane series sold by B. F. Goodrich Co., for example, Estane 5701, 5702, 5715, and 5707. Sensitizers include the diazoaromatic compounds, diazo-arylamine compounds, the para-diazo-diphenylamine compounds and either the aldehyde or acetal condensation products of these. Using the formaldehyde condensation product of p-diazo diphenylamine to sensitize Nylon copolymers is described by Hodgins.[45] The superpolyamine Nylon resin treated are the copolymers of Nylon 6 and polycaprolactam, Nylon 6/6 and hexamethylene diamine adipic acid, and Nylon 6/10 and hexamethylene diamine sebacic acid. A typical sensitized solution consists of 0.11 percent of the formaldehyde condensate of p-diazodiphenylamine, 0.94 percent superpolyamide nylon resin, 0.01 percent polyethylene gylcohol tertiary dodecylthioether, 17.15 percent water, 76.35 percent denatured

---

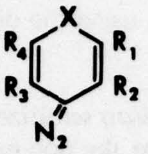
[43] **Maximilian P. Schmidt and Oskar Süs, "Quinone Diazides For Use In Reproduction Materials," U.S. Patent 2,994,608, 1 August 1961.**

[44] **Shashi B. Mainthia, "Diazo-Polyurethane Light-Sensitive Composition," U.S. Patent 3,660,097, 2 May 1972.**

[45] **George R. Hodgins, "Developer Composition For A Light-Sensitive Lithographic Plate," U.S. Patent 3,091,533, 28 May 1963.**

alcohol, and 5.44 percent furfuryl alcohol.

**Light sensitive diazo compounds with the general formula shown at the right are described by Poot[46] for the sensitization of alkali soluble resins.**



**X denotes either the sulfonyl group ($SO_2$) or a carbon-carbon bond; $R_{1-4}$ denotes hydrogen, but can preferably denote an electron-attracting substituent such as the halogens, cyanide, and nitrate functional groups, and also denotes an aryl or substituted aryl group.**

Examples of alkali soluble resins are the Novolaks and Resole resins described by Delzenne[47] and Silver.[48] Poot gives an extensive bibliography for the compounds he lists in his patent. One interesting patent by Cerwonka[49] states that the desensitizing dyes used in silver halide photography will photo-oxidize diazo compounds promoting radicals that initiate polymerization of unsaturated organic compounds or monomers in solution and in layers. Hence, dye-sensitized diazo compounds will photopolymerize vinyl monomers. Thus, $\text{Dye} + R - N_2^+ \longrightarrow \text{Dye}^+ + RN_2^{\bullet}$; $RN_2^{\bullet} \longrightarrow R^{\bullet} + N_2\uparrow$ in which $R^{\bullet}$ denotes a free radical that promotes the polymerization of the monomers. Examples of the desensitizing dyes include Rose Bengal, Erythrosine, Fluorescein, Amethyst Violet, Methylene Blue, Eosine, Brilliant Blue, Phenosafranine, Thionine, and Pinakryptol Green. The diazo compounds include p-toluene diazonium chlorozincate and p-toluene diazonium fluoborate. The radical sensitive monomers include vinylchloride, acrylamide, acrylonitrile, N-ethanol acrylamide methacrylic acid, acrylic acid, and calcium acrylate. Suitable supports include generally glass, metal, film, or paper. A typical coating consists of 1.000 gram polyvinylpyrolidone, K-90 (General Aniline and Film Co.), 0.250 gram N,N - methylene bisacrylamine (recrystallized twice from water), 0.098 gram Rose Bengal (F.W. 981), 0.200 gram p-toluenediazonium fluoborate, 0.08 ml (milliliter) of Wetsit spreading agent as a 10 percent solution, and water to make up 25·milliliters total solution. It is clear that the diazo compounds can and have been used to photosensitize different compounds and materials. It is not clear however that layers of these materials have been prepared or evaluated for holographic recording.

Through March 1972, over 90 patents treating aspects of diazo compounds were listed at the United States Patent Office, of which approximately one-third referenced the all-important formaldehyde condensation product of p-diazo diphenylamine salt or diazo resin. Although any of these diazo compounds may be suitable for the sensitization of monomers, resins, and materials such as gelatin, a number of the compounds and in particular the diazo resins are suitable for use as is without the addition

---

[46] Albert Lucien Poot, "Radiation-Sensitive Recording Material," U.S. Patent 3,493, 371, 3 February 1970.

[47] Gerard Albert Delzenne, "Production of Light-Sensitive Coatings For Use In the Manufacture of Copying Materials Such As Printing Plates," U.S. Patent 3,501,296, 17 March 1970.

[48] Julius L. Silver, "Printing Plate Composition," U.S. Patent 3,615,532, 26 October 1971.

[49] Edward J. Cerwonka, "Dye-Sensitized Photopolymerization Process," U.S. Patent 3,615,452, 26 October 1971.

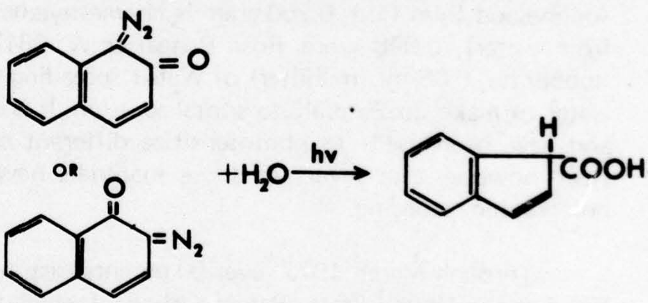
of polymerizable or tannable compounds. As of this date, no literature is known showing positive or negative results in using the diazo compounds in layers for holographic recording.

The photolysis products of the diazo sensitized compounds are insoluble in some solvents, such as water or alcohol, that the non-exposed photosensitive compound is soluble in. In that it is the photolysis products that remains following development, the diazo compounds are negative working with respect to exposure. Further, for the photolysis product to remain fixed to the supporting substrate the layer must be completely photolyzed if solvent development is to be undertaken. In this case, the resolution may be somewhat lacking as the layers are micrometer thick or greater.

There are mehtods to cause the non-exposed diazo compounds to react with different amines and phenol type compounds to form images typical of the diazotype process: but these methods are not of the photoresist type, and the literature is too extensive to treat at this time. Possibly, hardened gelatin may be sensitized with one of the diazo compounds much as in the manner with ammonium dichromate and may produce a holographic recording material that can be fixed with a solvent wash. But beyond these methods there are the ones that have met success in holographic working compounds that will be described next and applications will be found described in subsection entitled "Shipley's AZ 1350 (Positive Resist).

## DIAZO – OXIDE LAYERS.

**Oskar Süs[50] of Kalle AG writes about the nature of the photolysis products of diazo oxide compounds. Here the photochemical reaction of the diazo oxide promotes ring contraction, and with the presence of water the formation of an organic acid. Thus Süs proposes that**



It is the formation of the organic acid that is so strikingly different with the photosensitive diazo oxide. Instead of promoting corsslinking in some binder type material, the alkali soluble acid is formed that gives rise to a positive working photosensitive material with regards to exposure. It is the light-exposed regions then that are removed during development with alkali solutions, and the unexposed regions are left behind.

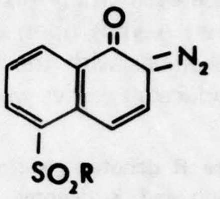
---

[50] Oskar Süs, "About the Nature of the Photolysis Product of the Diazo Compounds. Contraction of An Aromatic 6-Member Ring to A 5-Member Ring," *Liebigs Annalen der Chemie*, Vol. 556, 1944, pp. 65-83.

Consequently, unlike the negative working diazo layers, the diazo oxide layers do not have to be exposed through the bulk of the layer to give a fixed resist. Also, with thinner layers (even in the submicrometer region) plane wave interference gratings can be obtained with greater resolution or spatial frequency than the negative working resists.

The patent literature describes diazo oxide resists that are made up in alkali resistant resins to give a positive working plate. Levinos[51] describes a positive working layer in which the diazo oxide is dispersed in a water-insoluble, alkali-resistant binder resin that is coated on a layer of an acrylic resin that is alkali soluble. Good adhesion is reported to be the result of the two layers.

**The diazo oxides used are reported to be water insoluble, but soluble to the extent of a 1 percent solution in aliphatic esters, ketones, or alcohols and have the general formula shown at the right in which R denotes methyl, ethyl, phenyl, naphthyl, butyl, and benzyl ester of sulfuric acid.**



Examples of water-insoluble, alkali-resistant resins include phenol-modified coumarone-indene resins, polyvinyl acetate, polymethacrylate, polymethylmethacrylate, ethyl cellulose, cellulose acetate, cellulose propionate, and mixed esters. These resins will be soluble in the alcohol, ester, or ketone solvent to the extent of at least 1 percent solution and will resist development solutions. Developers consist of ethylene glycol, propylene glycol, glycerin, etc. Another patent by Hwang[52] describes a light-sensitive diazo compound prepared by reacting one mole of 3-amino-9-ethylcarbazole with one mole of 2-diazo-1-napthol-5-sufonyl chloride to produce diazo oxide that is soluble in cyclohexane. The compound is mixed one to one by weight with an alkali-resistant, water-insoluble polyvinyl acetate resin also soluble in cyclohexane. A water solution of sodium metasilicate and sodium alkyl aryl sulfonate that hydrolyzes to give an alkaline solution is used to develop the exposed layer. DiBlas and Franco[53] report using alkali-insoluble, alkali-permeable resins with the diazo oxides. Their examples include polymers obtained through copolymerizing acrylic, methacrylic, crotonic, and maleic entities that are unsaturated carboxylic acids with ethyl acrylate, butyl methacrylate, ethylvinyl ether, butylvinyl ether, phenylvinyl ether, vinyl acetate, styrene, vinyltoluene, indene, and acrylonitrile that are unsaturated monomers. The

---

[51] **Steven Levinos, "Offset Printing Plates," U.S. Patent 3,474,719, 28 October 1969.**

[52] **HoChien Hwang, "Diazo Compound for Lithographic Plates," U.S. Patent 3,544,323, 1 December 1970.**

[53] **Umberto DiBlas and Simone Franco, "Offset Printing Positive Diazo Presensitized Matrixes Containing Photosensitive Quinone Diazide and A Resin Binder," U.S. Patent 3,551,154, 29 December 1970.**

copolymers formed are crosslinked with crosslinking agents, for example, epoxides, ethylene imine, isocyanates, hexamethylene diisocyanate, diphenylmethane-4, 4' diisocyanate, triethylene imino phosphine oxide, and triisocyanate. It is the crosslinked polymers that are alkaline-insoluble but swell in alkali. The carboxyl group (—COOH) content appears to be from 3 to 13 percent free groups. The sensitizers used were o-diazonaphthoquinone-5-sulfonic acid esters and benzoquinonediazide-2-sulfonic acid.

Perhaps of lesser importance than the alkali-insoluble, alkali-permeable resins used with the diazo oxides are the alkali-soluble resins, such as the Novolaks and Resoles. The alkali-soluble resins may produce layers that are difficult to develop because even when mixed with the diazo oxide, the resins tend to dissolve in the unexposed regions upon development. Still, Laridon[54] proposes use of 1, 2-diazo oxide derivatives with the following general formula to sensitize alkali soluble polymers to produce a positive working photosensitive layer.

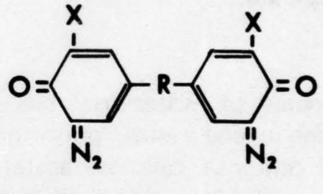
Here R denotes a sulfone, -$CH_2$ or cycloaliphatic group and X denotes -H, halide, - $NO_2$, or alkyl group of one to four carbon atoms. Examples given include:

bis (6-diazo-2,4-cyclohexadien-4yl-l-on) methane.

bis (6-diazo-2,4-cyclohexadien4yl-l-on) phenylmethane.

2,2 bis (6-diazo-2,4-cyclohexadien-4yl-l-on)-propane.

2,2 bis (2-bromo-6-diazo-2,4-cyclohexadien-4yl-on)-propane.



The procedure used to prepare the diazo oxide is given. The product is mixed in a 1:1 ratio with the Novolak resin and dissolved in a solution consisting of 3 milliliters of glycol ethyl ether and 2 milliliters acetone. A 1 percent solution is obtained in the oxide. Development is carried out with 5 grams of $Na_3PO_4 \cdot 12H_2O$ and 15 grams of NaCl in 100 milliliters of water. The layer may be post-treated with a 1 percent solution of $H_3PO_4$. In a second patent, Laridon[55] sensitizes Novolak resin with 1,2-naphthoquinone-2-diazo-5-fluorosulfonyl as before to produce a positive working layer that is developed with a $Na_3PO_4$, NaCl solution and post-treated with 1 percent $H_3PO_4$ solution. The layer thickness is reported to be 2 micrometers. Delzenne[56] proposes using the diazo-oxindoles with the following general formula to sensitize the Novolak resins, which are preferred.

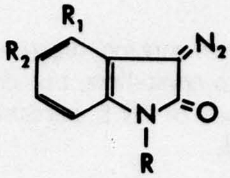
---

[54] Urbain Leopold Laridon, "Copying Material for Use In the Photochemical Preparation of Printing Plates," U.S. Patent 3,494,767, 10 February 1970.

[55] Urbain Leopold Laridon, "Copying Material for Use In the Photochemical Preparation of Printing Plates," U.S. Patent 3,495,979, 17 February 1970.

[56] Gerard Albert Delzenne, "Production of Light-Sensitive Coatings For Use In the Manufacture of Copying Materials Such as Printing Plates," U.S. Patent 3.501,296, 17 March 1970.

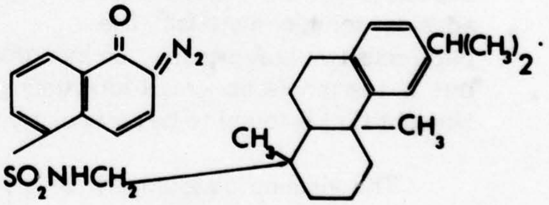
**This is the general formula to sensitize the preferred Novolak resins. The R denotes -H, an alkyl, aryl, alkaryl, aralkyl or acyl group and $R_1$ and $R_2$ denotes either -H or a fused benzene ring.**



Examples of the diazo-oxindoles are as follows: 3-diazo-oxindole, 1-methyl-3-diazo-oxindole, 1-benzoyl-3-diazo-oxindole, and 1-cinnamoyl-3-diazo-oxindole. A solution of 3 milliliters acetone. 50 mg (milligrams) of the compound 1-methyl-3-diazo-oxindole, and 50 milligrams of Novolak resin is applied to a suitable substrate (layer thickness is 3 micrometers). The layer is exposed and developed with 5 percent $Na_3PO_4$ solution. The layer can be post-treated with a 1 percent $H_3PO_4$ solution. Whitear and Fry[57] treat the addition of the photochromic material, 3 pyridyl-sydnone, 2,2',4'-di-nitrobenzyl pyridine, to 1,2-diazonaphthoquinone or 1,2-diazobenzoquinone and to the phenol formaldehyde resin mixtures of these. A visible image is produced on the layer following simple exposure.

Kobayashi[58] has found that low molecular weight diazo and diazo oxide compounds produce crystalline deposits on layers reducing the mechanical strength of the images formed, and incorporating such compounds in resin succeeds in reducing the sharpness of the light sensitive layer in development. Further, he points out that other high molecular diazo and diazo oxide compounds exhibit poor adhesion to certain substrates (e.g. aluminum plates). The high molecular weight, light-sensitive materials he proposes are free of the problems in image sharpness and adhesion. They are prepared using commercially available sulfonic acid of diazo oxide (e.g. 2-diazo-1-naphthol-5-sulfonic acid, 2-diazo-1-naphtol-4-sulfonic acid) in the following manner. First, the sulfonic acid chloride is prepared by treating the sulfonic acid with chlorosulfonic acid. Second, the sulfonic acid chloride (e.g. 2-diazo-naphthol-5-sulfochloride) is dissolved with polyhydroxy phenyl, and a 10 percent aqueous solution of $K_2CO_3$ is added slowly. The $K_2CO_3$ neutralizes the hydrochloric acid formed driving the reaction to completion.

**A solution of the resulting compound (i.e. diazo polyhydroxy phenyl ester resin) is dissolved in cyclohexane under yellow light conditions and used to coat a suitable substrate. Like Kobayashi, Deutsch and Loprest[59] prepared a high molecular weight diazo of the formula N-dehydroabietyl-6-diazo-5(6H) -oxo-1-napthalene sulfonamide as shown**



---

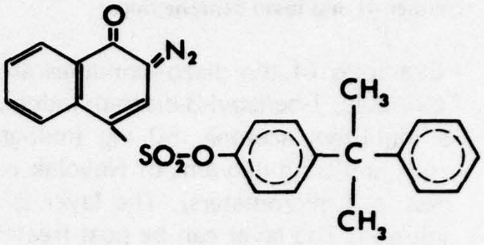
[57] Brian R.D. Whitear and Douglas James Fry, "Litho Plate," U.S. Patent 3,589,898, 29 June 1971.

[58] Kesanao Kobayashi, "Light-Sensitive Lithographic Plate," U.S. Patent 3,635,709, 18 January 1972.

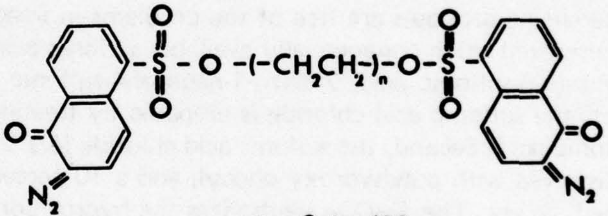
[59] Albert S. Deutsch and Frank J. Loprest, "Positive-Working Diazo-Oxide Terpolymer Photoresists," U.S. Patent 3,637,384, 25 January 1972.

The positive-working diazo oxide incorporated in a resinous terpolymer has little tendency to crystallize, but does form excellent films. An example of the terpolymer is a mixture of 57.5 percent ethylacrylate, 32.6 percent styrene, and 9.9 percent acrylic acid.

**Süs and Uhlig[60] propose still another high molecular weight compound of the form shown. It is produced upon condensing cumyl phenol with the sulphonyl chloride of diazo oxide.**



The high molecular weight compound has high solubility (15 percent solutions reported) and good uniform chemical composition. The cumyl phenol ester of 1,2-naphthoquinone diazide-(2)-4-sulfonic acid and Novolak resin are dissolved in glycol monoethylether and coated on suitable substrates. Rauner, et al [61] offers light-sensitive polymers that avoid the crystallization problems of sensitizers dissolved in binder resins and have minimal brittleness and inflexible properties. Here polyalkylene glycol (e.g. Union Carbide's Carbowax 600, 1000, and 4000) is dissolved in pyridine and treated with 1,2-naphthoquinone-2-diazide-5-sulfonyl chloride, while shielded from light. The pyridine is neutralized with dilute HCL, and the aqueous solution is extracted with methylene chloride. Upon washing the extracted solution with water, drying, and reducing the volume, a viscous liquid is isolated that is composed of polymers of the form shown on the right. The polymers undergo essentially no crosslinking upon exposure, but are converted to alkaline soluble material. The photosensitive polymer may be incorporated in one of the Novolak or Resole Resins, but a thermoplastic cresol-formaldehyde resin (Alnovol 429K sold by American Hoescht Co.) is found to be particularly useful.



n = 8 to 400

The alkaline development of a positive working 1,2-diazo oxide light-sensitive

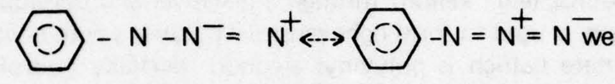
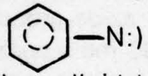
---

[60] Oskar Süs and Fritz Uhlig, "Naphthoquinone Diazide Sulfonic Acid Ester," U.S. Patent 3,640,992, 8 February 1972.

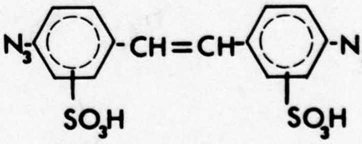
[61] Frederick J. Rauner, J.A. Arcesi, and J.R. Guild, "Light-Sensitive Quinone Diazide Polymers and Polymer Composition," U.S. Patent 3,647,443, 7 March 1972.

layer is well known. Lawson[62] has found that some polar organic solvents accomplish the same end. The preferred solvents include 2-ethyl hexanol, 1-octanol, 2,6-dimethyl-4-heptanone, 6-methyl-3-heptanone, n-hexylacetate, diethylphthalate, diethylcarbonate, 3-methyl-2-pentanone, and industrial ethanol. Development time is 5 minutes.

Holstead[63] discloses 1,2-diazo oxide, trihalomethanes that produce layers without additional resinous materials and that have visible images requiring no development upon simple exposure to UV light through a film image. Examples include 5,6-dihydro-6-diazo-2-tribromomethyl quinoline-5-one, and 5,6-dihydro-6-diazo-2-trichloromethyl quinoline-5-one. Coating thickness are on the order of 2.5 to 75 um (mircometers).

AZIDE LAYERS. By following the discovery of the photosensitization effects of the diazos, certain organic azides, with the resonance structure  were found to photolyze, promoting insolubilization of resins and materials such as gelatin. Unlike their inorganic counterparts, the organic azides demonstrate good stability with minimum of decomposition in the colloidal layers in which they may be incorporated. Although the subject is still controversial, exposure to light is believed to result in the formation of nitrogen and of a free radical from the organic azide. The free radical generated (namely the arylnitrene (  ) couples with any adjacent molecule, thus promoting crosslinking of the colloidal material resulting in its insolubilization. This is particularly the case when the bis-azides (i.e. organic azides with two azide groups in the molecule) are used. The class of organic azide compounds will be described next.

Hepher[64] points out in his photoresist story that 4,4'-diazidostilbene disulphonic acid promotes very stable layers and good photo crosslinking when added to gelatin. This compound has the structural formula shown on the right and we see that it is a bisazide. Merrill and Unruh[65] of Eastman Kodak Co. offer new polymeric azides in which carboxyl or sulfonic acid groups are incorporated into the polymer chain so as to impart solubility of the light sensitive polymer in dilute alkali or ammonia solutions.



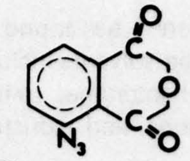
---

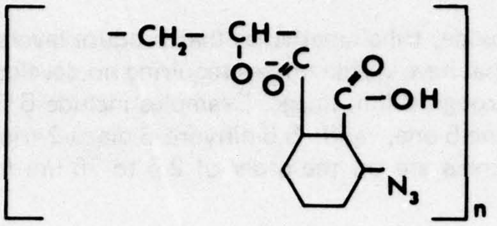
[62] **Leslie Edward Lawson, Frank E. Smith, and Peter John Smith, "Solvent Development of Light Sensitive Diazo Layers," U.S. Patent 3,634,086, 11 January 1972.**

[63] **Colin Holstead, Abbotts Langley, and Wojciech Maria Prezezdziecki, "Diazo Compounds and Photographic Elements," U.S. Patent 3,592,646, 13 July 1971.**

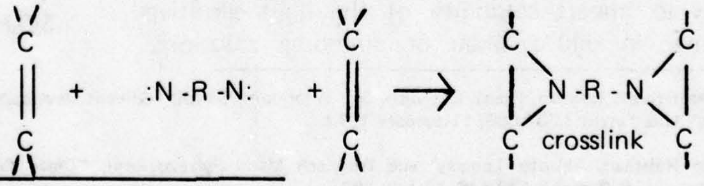
[64] **M. Hepher, "The Photo-Resist Story - From Niepce To The Modern Polymer Chemist," *J. of Photographic Science*, Vol. 12, 1964, pp. 181-190.**

[65] **Stewart H. Merrill and Cornelius C. Unruh, "Azidophthalic Anhydrides," U.S. Patent 3,002,003, 26 September 1961.**

Thus, when polyvinyl alcohol is treated with  at $50^{\circ}$ to $60^{\circ}$ C one obtains a sensitized polymer resin of the form illustrated on the left in which 'n' is a large number. The product is soluble in dilute $NH_3{\cdot}H_2O$, dilute NaOH, and dioxane. Dissolved in dilute $NH_3{\cdot}H_2O$, the product is coated on a suitable substrate, exposed to carbon arc or other suitable UV source (e.g., xenon) through a negative, and developed with dilute alkali. The preparation is used to form light sensitive polymers with completely hydrolyzed poly vinyl acetate (which is polyvinyl alcohol), partially hydrolyzed cellulose acetate, gelatin, ethylene-vinyl alcohol copolymer, and styrene-maleic anhydride heteropolymer. Takeishi and Okawara[66] treat preparation of azide containing polyvinyl chloride (PVC). The reaction is unusual in that PVC is not notably susceptible to nucleophilic substitution reactions. Sodium azide is added to a solution of PVC in dimethylformamide at $60^{\circ}$C. Upon stirring the suspension for approximately 15 hours, 60 mole percent conversion of the chloride to azide groups is obtained, and a gel formation is observed. At higher temperatures, 80 mole percent conversion was seen. The azido-PVC is photosensitive in that crosslinking is promoted upon irradiation with UV light. The material was thermally stable up to $100^{\circ}$C. Rapid decomposition was observed spectroscopically at $140^{\circ}$C. Efros et al.[67] find that bisazides, particularly bisazides containing carbonyl groups in the molecule, serve as crosslinking agents for polymers illuminated with actinic light. The polymers used contain double bonds (e.g. cyclorubber with molecular weight equal to 7,000 to 8,000 grams per mole). The proposed reaction with double bond polymers is described as follows:



$$N_3\text{-}R\text{-}N_3 \xrightarrow[-N_2]{h\nu} \underset{\text{azidonitrene}}{N_3\text{-}R\text{-}N{:}} \xrightarrow[-N_2]{h\nu} \underset{\text{dinitrene}}{{:}N\text{-}R\text{-}N{:}}$$



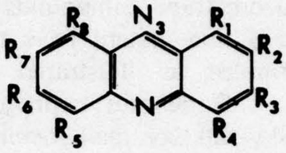
---

[66] Makoto Takeishi and Makoto Okawara, "Synthesis and Reaction of Polyvinyl Chloride Containing Azide Group," *J. of Polymer Science, Part B*, Vol. 7, No. 3, March 1969, pp. 201.

[67] I.S. Efros, T. Urres, K.S. Lyalikov, K.A. Kovalera, "The Mechanism of the Light Hardening of Polymers With Azides," Translated from Russian by U.S. Army Foreign Science and Technology Center, AD 727-964, July 1971.

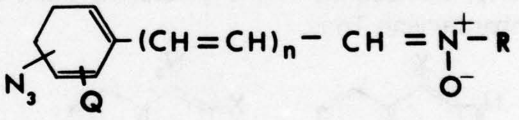
Efros states that use of known free radical initiators (e.g. p-azidoacetophenone) did not promote increased crosslinking. Further, the addition of free radical inhibitors (e.g. hydroquinone and N-phenyl-B-naphthylamine) up to 5 percent by weight of the bis-azides, did not noticeably alter the rate of crosslinking. He concludes then that the crosslinking reaction does not proceed by a free radical reaction.

Reyolds[68] et al. offers 23 derivatives of 9-azidoacridines with the general formula illustrated on the right as being light sensitive. Here $R_{1-8}$ may be H, halogen. alkyl, aryl, alkoxy, carboalkoxy, $-NH_2$, $-NO_2$, -CN, and any two consecutive positions can represent the atoms necessary to complete an aromatic ring. The derivatives may be used to sensitize water permeable, hydrophilic colloids used in photomechanical processes in the spectral range 208 to 540 nanometers.

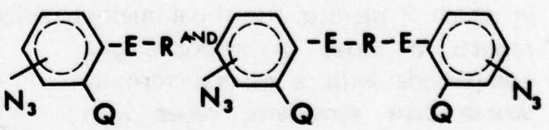


Ruckert[69] of Kalle AG has been awarded three patents covering a total of 86 novel azido compounds, namely 9 azido-nitrone compounds, 38 azido styryl compounds, and 29 azido-azomethine compounds. Certain of the compounds are bisazides. The compounds may be used to sensitize either the alkali-expandable or the alkali-soluble resins, such as the Novolaks. The azido nitrones have the general formula illustrated on the right in

which Q = H or other substituent
R = isocyclic aromatic or heterocyclic aromatic either substituted or not
N = 0 or 1



The azido styrl compounds have the general formulae as illustrated in which the rings denote benzene, naphthalene, anthracene, pyridine, or quinoline rings. Q denotes hydrogen



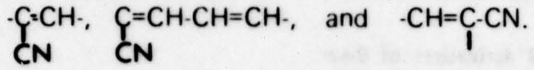
---

[68] George A. Reynolds, "Photosensitive Compounds and Elements," U.S. Patent 3,519,424, 7 July 1970.

[69] Hans Ruckert, "Reprographic Copying Composition," U.S. Patent 3,455,914, 15 July 1969. "Reprographic Copying Composition," U.S. Patent 3,539,559, 10 November 1970. "Azido Azomethines For Reprographic Copying Compositions," U.S. Patent 3,558,609, 26 January 1971.

or other substituent (-OH, akyl, alkoxy, dialkyl, $-NH_2$, $-NO_2$, X, and $-N_3$). R denotes an isocyclic aromatic or a heterocyclic aromatic group, or a carbonyl group in the free acid form or in the form of an ester, amide, or nitrite that is attached to the cyanomethyl group of group E when E is -CH=C-CN.

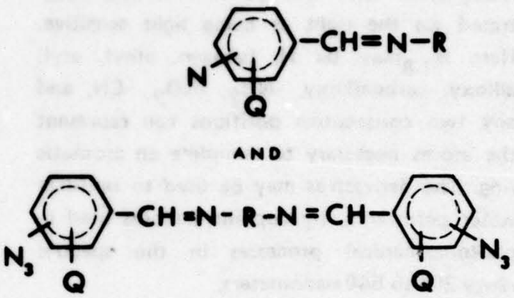
E denotes ethylenically unsaturated entity of the form -CH=CH-,



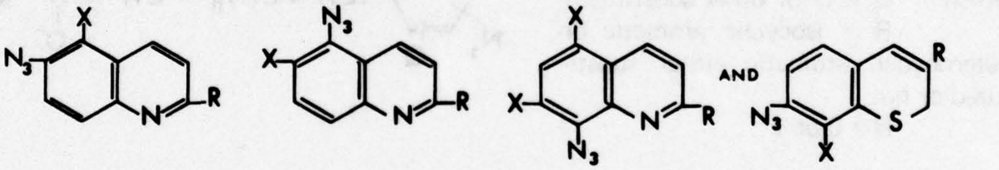
$$-\underset{CN}{C}=CH-,\quad \underset{CN}{C}=CH-CH=CH-,\quad \text{and}\quad -CH=\underset{|}{C}-CN.$$

The azido azomethine compounds of the third and final patent have the general formulae as illustrated in which the Q denotes hydrogen, hydroxyl, alkyl, alkoxy, dialkylamino, and azido groups.

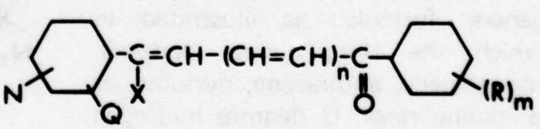
R denotes isocyclic aromatic or heterocyclic aromatic group, or substituted isocyclic aromatic or heterocyclic aromatic group.



One of the more interesting aspects of the azide photosensitive compounds is the adjustment in the spectral absorption, which may be obtained, that is dependent upon chemical structure. Holstead et al.[70] have found that incorporation of the trihalomethane group (e.g. $CBr_3$) within the azide molecule enhances the photosensitivity. Compounds of the general formulae shown next, exhibit this photosensitivity enhancement. Thus,



in which R denotes the trihalomethyl radical, and X is a halogen atom. Kalle AG[71] reports a series of azidochalcone compounds with a general formula whose peak sensitivity varies with wavelength from 314 to 393 nanometers.



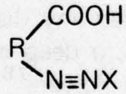
---

[70] Colin Holstead, Abbotts Langley, and Wojciech Maria Prezezdziecki, "Azide Sensitizers and Photographic Elements," U.S. Patent 3,617,278, 2 November 1971.

[71] Kalle AG, "Improvements In and Relating to Reprographic Materials," British Patent 1,223,570, 24 February 1971.

Ruckert[72] has made a similar find for the series of his novel azido azomethine compounds. Their peak absorption occurs from 292 to 401 nanometers. A word of caution is needed because possibly the peak spectral sensitivity of these compounds may not exactly coincide with the reported absorption maxima. Still, we have seen that there must be absorption before there can be spectral sensitivity, and quite often the spectral sensitivity and absorption maxima do coincide.

We have seen that there is extensive literature with hundreds of photosensitive compounds that can be used as is or incorporated in many different resins or materials, such as gelatin, to produce photosensitive materials that can be used as photoresists or as layers whose exposure to actinic light produces variations in absorption or refractive indices. There are hundreds of diazo, diazo oxide, and azide compounds remaining to be invented, and perhaps many of them will prove to be suitable as holographic recording materials.

DIAZO GELATIN. The introduction of diazo compounds into colloidal protein layers, such as gelatin layers, produced photosensitive layers that initially trap the nitrogen evolved from the diazo compounds. Different effects may be produced in the layer depending upon composition of the layer and what is done to the layer during and following exposure to actinic light. For example, Zemp[73] found that in his hardened diazo layers the gelatin became white and opaque from the collection of small nitrogen bubbles within the layer as the result of the photolysis of the diazo compound. Upon immersion of the photolyzed layer in hot (70$^{\circ}$C) water, the exposed regions could be developed out by rubbing gently with a cotton pad. A positive relief image of the original, in which the unexposed regions remained, is found. The thickness of the light sensitive layer ranges from 1 to 2500 nanometers or more, and the diazo can vary from 0.1 to 5.0 parts per 100 by weight of protein colloid. The diazonium salts have the general formula  $R\begin{smallmatrix}\diagup COOH\\ \diagdown N\equiv NX\end{smallmatrix}$ in which X is an anion of acid (e.g. $C1^-$, $SO_4^{=}$, $NO_3^-$, $BF_4^-$, $SO_3N_2^-$, and $SO_3K^-$), and R denotes a substituted benzene or naphthalene entity. The popular compounds referenced in the patent are o-carboxybenzene-diazonium chloride or sulfate. The diazonium salt can be introduced in the coating solution either at the time the layer is being coated or later by soaking the colloidal protein layer in an aquous and/or organic solvent solution containing the diazo compound. Peterson and Fabian[74] found that following exposure to actinic light the diazotized gelatin layers can be heated and pressure deformed next to thermo-

---

[72] Hans Ruckert, "Azido Azomethines For Reprographic Copying Compositions," U.S. Patent 3,558,609, 26 January 1971.

[73] Rene Robert Zemp, "Process For Producing Images," U.S. Patent 2,729,562, 3 January 1956.

[74] Willard D. Peterson and Robert W. Fabian, "Photographic Reliefs Made By Means of Transfer Intermediaries Which Produce Gas Upon Irradiation," U.S. Patent 3,093,478, 11 June 1963.

plastic sheets to produce relief records in both the sensitized gelatin layers and the thermoplastic sheets. Upon indurating and separating, two relief records are obtained that correspond to the light image used to expose the sensitized gelatin layer. Again, it is the encapsulated nitrogen gas in the gelatin layer that expands in the heat softened matrix producing the records. The gelatin relief can be permanently hardened by heating to temperatures above 250°C. Diazo compounds mainly sensitive from 350 to 450 nanometers include p-diazodiphenylamine sulfate, p-diazo diethylaniline zinc chloride, p-diazo ethyl methyl aniline zinc chloride, and others. The support includes such materials as glass, acetate film, or metal. The thermoplastic receptor body of importance is comprised of cellulose acetate. The relief records have application in offset and letterpress printing of conventional line and halftone imagery and in preparing Braille records. Unlike Zemp, personnel with Philips Lamps Limited[75] found that by controlling the light intensity during exposure, layers were obtained that were not turbid from gas evolution. This occurs when the light is too intense and when the intensity is sufficiently reduced; a layer is produced in which the unexposed regions could be removed with a cotton pad after soaking in running water for a few hours. Casein as well as egg albumen and gelatin layers are suggested that can be prepared on glass by treating the same with a 5 percent solution of the respective colloidal protein containing ammonia water. After drying, the casein plate is soaked for 3 minutes with an aqueous solution of 5 percent by weight 1-hydroxy-2-diazoniumbenzene-4-sulphonic acid, 13 percent by weight copper nitrate (m.w. 295), and 5 percent by weight of chrome alum. The plate is then bathed 5 to 10 seconds in 94 percent alcohol and air-dried. Exposure is made for 10 to 15 seconds to a 2-kilowatt mercury vapor lamp at 40 centimeters. The plate is then bathed for 20 seconds in a solution of 1 percent by weight of potassium chromate in water at 50°C. The print is then developed and dried. The diazonium compound produces a photolyzed product that acts to tan the colloidal protein. In the presence of water, the product formed is primarily a phenol that in turn can also oxidize any diazonium compound remaining to form a colored azo dye compound. Thus, a deep brown-violet image may be observed. In addition to the above individuals, Powers[76] also found that the release of gaseous nitrogen into the colloidal protein layer would produce large blisters if the layer is immersed in water immediately following the exposure. The blisters were observed in gelatin layers sensitized with either diazo or azide sensitizing compounds. Powers found that the problem could be avoided by subjecting the exposed diazo or azide sensitized sheet to a relatively high degree of vacuum as in a vacuum printing frame. A vacuum in excess of 508 millimeters of mercury is simply applied for a period of time dependent on the emulsion thickness, the amount of exposure, and the concentration of the sensitizer in the layer. Usually 5 to 20 minutes is sufficient time to apply the vacuum to the exposed layer.

---

[75] Philips Lamps Ltd., London, "Improved Method of Producing Photographic Contrasts By Means of A Diazonium Compound," British Patent 534,341, 5 March 1941.

[76] Augustin J. Powers, Jr., "Development of Diazo and Azide Sensitized Colloids," U.S. Patent 2,690,968, 5 October 1954.

The impact of using the diazo and perhaps even the azide compounds to sensitize colloidal protein or resin binder matrices is that sufficient nitrogen gas may be evolved in an imagewise fashion to produce fractures in the emulsion corresponding to the light pattern of a holographic interferrence pattern and thus to enhance the diffraction efficiency obtained. The effect may be controlled by adjusting sensitizer concentrations in the emulsion, the emulsion thickness, the light intensity, the vacuum, and the temperature of any developing media.

UNHARDENED DICHROMATED GELATIN. Of the two, hardened and unhardened dichromated gelatin, the latter is used as a photoresist. The unhardened gelatin may be developed out following photolysis leaving the tanned resist behind on a suitable substrate. This then would produce holographic plates with a surface relief typical of a surface phase hologram. The hardened dichromated gelatin, prepared by immersing cleared photographic plates in solutions of dichromate salts, does not develop out the unexposed gelatin, and it produces holograms as variations in refractive indices of the exposed material. A volume phase hologram is obtained. This will be treated in detail later.

Actually, photosensitive colloidal proteins sensitized with dichromate salts have been known in the printing industry for decades. The colloidal proteins include not only gelatin but also egg albumen; casein, a milk product; and zein, made from corn. These have been used in photogravure or deep etch plate printing or in planographic printing (e.g. offset lithography). Interestingly, the more recent patent literature occurs in the late fifties and early sixties. Then the literature was inundated with patents treating the diazos, diazo oxides, and azides. These compounds essentially usurped the dicrhomate sensitized colloidal proteins because, as we see in Rouse et al.[77] gelatin sensitized with diazo compounds, i.e. p-quinone-diazide sulphonic or carboxylic-acids, could be stored for suficient time without deterioration in photosensitivity or printing quality so they could be sold as commercial articles.

Rouse et al. described both diazo and dichromated gelatin in their patent. It is the dichromated unhardened gelatin that will be treated here. Thus, gelatin that is suitably pigmented and plasticized is coated on a suitable substrate to give a dry film coating of approximately 50 micrometers (2 mils) thickness. This film may be stored indefinitely prior to sensitization. To sensitize the film, it is immersed in a 1 percent potassium bichromate solution at 65°F for 2 minutes. The excess sensitizing solution is squeegeed off, and the layer is dried for 30 minutes by using warm dry air from a heater fan device. For photogravure, exposure is made through a diapositive to a suitable actinic light source. Development is carried out in water at 110°F to dissolve away the unexposed, untanned gelatin. The remaining resist is chilled with cold water

---

[77] **Edward Rouse, "Improvements In or Relating To Photogravure Processes," British Patent 859,781, Patent Provisional Specification No. 33841, 25 January 1961.**

and air-dried. A preparation for a sensitized coating containing a diazo compound that could well be substituted with a requisite amount of potassium and/or ammonium dichromate is given as follows: water, 750 cubic centimeters; gelatin, 250 grams; dispersed inert pigment, 25 grams; sulphonic acid salt of p-quinone diazide, 60 grams; glycerine, 60 grams; saponin, 5 grams; wetting agent (Imperial Chemical Industries, LTD., "Calsolene HS"), 2.5 cubic centimeters. After coating and drying, the layer is sensitive to light and may be processed as described before. Pries[78] describes an improved dichromated albumen coating solution that will not separate in standing or in use. As an example, he prepares a 6° Baume albumen solution as follows: Egg albumen (scales), 115 grams (4 ounces); water, 600 cubic centimeters (20 liquid ounces); and 58 percent ammonium hydroxide, 30 cubic centimeters (l liquid ounce). The albumen is dissolved in the water, and then the ammonia water is added. Additional water may be added to adjust the specific gravity to 6° Baume. The resulting solution is strained through multiple layers of cheesecloth and stored in bottles. An ammonium bichromate solution, 10° Baume, is prepared from water, 360 cubic centimeters (12 liquid ounces); ammonium phosphate (dibasic), 14.2 grams (½ ounce); ammonium nitrate, 14.2 grams (½ ounce); and ammonium dichromate, 28.4 grams (1 ounce). In preparing this solution, each reagent is added and dissolved in turn. As before, additional water may be added to make up the 10° Baume solution if the specific gravity is too high. The plate coating solution is made up as 2 parts (50 cubic centimeters) of the albumen solution and one part (25 cubic centimeters) of the dichromate solution. About 270 cubic centimeters of water (9 liquid ounces) is added to make the resulting solution 3° Baume. The coating solution is then filtered through cheesecloth and bottled. The coating solution can be applied to a suitable substrate using a whirler. Different ratios of albumen to dichromate solution may be tried, and the specific gravity of the resulting coating solution may be made as low as 2.5 Baume. The ammonium phosphate and the ammonium nitrate preserve the sensitized albumen solution so that there is no deterioration before use. Sensitized layers can be set aside for several hours in the dark with no adverse effect from high temperatures or humidities. Caton[79] describes a fractionated casein coating sensitized with dichromate that is the basis for his patent. A casein stock solution is first prepared by mixing the following: milk casein (trade name Protovac), 11.6 percent; 27 percent ammonium hydroxide, 1.5 percent; and water, 86.9 percent by weight. The casein is stirred into three-fourths of the water and mixed for 40 minutes while rising the temperature to 135°F. Discontinue the heating, and add the ammonia water while mixing for an additional 45 minutes. The remainder of the water is then mixed into the casein until a uniform consistency is obtained. A gelatin admixture is prepared by dissolving 0.2 percent by weight of gelatin into 99.8 percent water at 150°F. The ammonium dichromate solution is prepared by mixing the following: ammonium dichromate,

---

[78] **Lawrence L. Pries, "Light Sensitive Plate Coating," U.S. Patent 2,858,214, 28 October 1958.**

[79] **Thomas R. Caton, "Light Sensitive Coating and the Method For Its Production," U.S. Patent 2,921,852, 19 January 1960.**

7.86 percent; 27 percent ammonia water, 17.21 percent by weight; water, 74.93 percent. To produce an intermediate mixture, a ratio of 100:11:21 by volume of the respective solutions, i.e. the casein stock solution the gelatin admixture and the ammonium dichromate solution, are mixed together. Although the intermediate mixture is a usable coating composition, the mixture is further treated with a concentrated mineral acid to produce a better coating composition. The acid added is an amount less than the quantity needed to fully neutralize the ammonia present, and the fractional part of the casein that then precipitates out is filtered off. Thus about 30 milliliters of concentrated nitric acid per gallon of the intermediate mixture is added, and following filtering off the precipitate, a quantity of ammonia is added to restore the pH of the solution to its original value of 9.0. The fraction of casein removed by this method is believed to weaken the structural strength of the remaining casein. Thus, the coating solution with the fraction removed now gives a longer press run when fully processed.

The final description illustrates that ammonium dichromate can be used to sensitize other than colloidal protein layers. Boersma[80] has shown in his patent that the dichromate can be used to make polyvinylbutyral resin photosensitive. He also reports that the same may be accomplished with diazonium compounds, although the example he gives is not that of a diazonium compound but that of an amine from which a corresponding diazo may be chemically prepared. Again, and in closing the subsection on unhardened dichromated gelatin, the patent literature demonstrates the loss of interest in dichromate sensitized coating materials in preferrence for the more chemically stable diazo sensitized coating materials. Since about 1962, the U.S. patent literature is void of any patents treating photoresists or planographic printing layers containing dichromates.

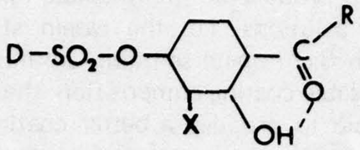
SHIPLEY'S AZ 1350 (POSITIVE RESISTS). Perhaps the most descriptive treatment of Shipley's AZ 1350 photoresists in the nonpatent literature will be found in Clark's[81] paper in which he gives a brief review of the chemical composition of the more important photoresists used in microelectronics. The U.S. patents assigned to Shipley Company, Inc. best define the chemical composition of the positive photoresist materials, and this patent literature will be described here in the belief that it does reveal the chemical nature of Shipley's AZ 1350 photoresists.

---

[80] Theo Tjalke Boersma, "Method of Manufacturing Metallic Patterns," U.S. Patent 2,819,164, 7 January 1958.

[81] Kenneth G. Clark, "Photoresist Techniques in Microelectronics," in R.J. Cox (Ed.), *Non-Silver Photographic Processes*, New York, Academic Press, 1975, pp. 249-273.

The earlier patent assigned to Shipley Company, Inc.[82] describes coatings containing naphthoquinone-1 2-diazide-sulfonic acid esters of the diazo oxide class of compounds that, in addition, have an OH group or an esterified OH group that is in a neighboring position to a carbonyl group as seen in the representative structural formula. Here D denotes the naphthoquinone-1,2-diazide radical, X is hydrogen or hydroxyl, R is hydrogen, $OR_1$, $NR_2R_3$, or a substituted or unsubstituted alkyl, aryl or heterocyclic radical, $R_1$ is alkyl or aryl, and $R_2$ and $R_3$, which may or may not be identical, are hydrogen, alkyl, or aryl radicals.



In their earlier work, Neugebauer and Endermann[83] of Kalle AG supposed that such esters with free hydroxyl groups present in their molecules would be dissolved in the alkaline developers used to dissolve their respective acidic photolysis products. They soon learned, however, that the OH group is linked to the adjacent carbonyl group through a hydrogen bond denoted by the stippled bond in the above formula and that, thus bonded, the OH group was not too susceptible to alkaline attack. The compounds are insoluble in water but are soluble in certain organic solvents at room temperature. The naphthoquinone-1,2-diazide-sulfonic acid esters produce extremely uniform coatings with alkali soluble resins and, as we will see with alkali-resistant resins that are free of crystallites and that adhere very well to metal substrates used in relief and intaglio printing plates. Schmidt,[84] Endermann et al.[85] and Neugebauer et al.[86] have obtained patents describing many diazo oxide compounds with the above description and representative structural formula. Whereas the Kalle personnel found that the naphthoquinone-1,2-diazide-sulfonic acid ester produced exceptional coatings with alkali-soluble resins (e.g. the phenol-and cresol-formaldehyde novolaks sold under the trade name Alnovol), the Shipley people learned that these coatings can be substantially improved in their resistance and thickness properties with the inclusion of alkali-resistant resins (e.g. polystyrene; copolymers of p-methylstyrene and vinyl

---

[82] Thomas L. Steinhoff, Charles R. Shipley, Jr., and John A. MacDonald, "Light-Sensitive Naphthoquinone Diazide Composition and Material Containing an Alkali Insoluble Polymer," U.S. Patent 3,402,044, 17 September 1968.

[83] Wilhelm Neugebauer and Fritz Endermann, "Naphthoquinone Diazide Lithographic Material and Process of Making Printing Plates Therewith," U.S. Patent 3,106,465, 8 October 1963.

[84] Maximillian Paul Schmidt, "Process of Making Printing Plates and Light Sensitive Material Suitable For Use Therein," U.S. Patent 3,046,118, 24 July 1962, Formulae 20 and 21.

[85] Fritz Endermann, Wilhelm Neugebauer, and Maximilian Karl Reichel, "Light Sensitive O-Quinone Diazides and the Photomechanical Preparation of Printing Plates Therewith," U.S. Patent 3,148,983, 15 September 1964.

[86] Wilhelm Neugebauer, Fritz Endermann, and Maximilian Karl Reichel, "Etchable Reproduction Coatings On Metal Supports," U.S. Patent 3,201,239, 17 August 1965.

toluene; the polymeric reaction product of melamine, formaldehyde, and a lower alkyl monoalcohol; the polymeric reaction product of benzoquanamine, formaldehyde, and a lower alkyl monoalcohol; and sucrose benzoate) in the formulation. The alkali-resistant resins are those resins whose thin film (i.e. 0.625 micrometer thick) will withstand treatment with 0.4N KOH or preferably 1. 0 N KOH for 10 minutes at 30°C. without visible attack as seen by the unaided eye. Fine, light-sensitive resist layers are prepared 200 nanometers thick from the following materials: 168 liters ethylene glycol monomethylether (99 percent pure), 21.0 kilograms alkali soluble, phenol-formaldehyde novolak resin (Alnovol 429 K), 21.0 kilograms solid copolymer containing 25 to 35 percent by weight a-methyl styrene and 75 to 65 percent by weight vinyl toluene (as described in U.S. Patent 3,000,868), 21.0 liters butylacetate (90 to 92 percent pure), 21.0 liters xylene, and 6.3 kilograms of sensitizer (example 20, U.S. Patent 3,046,118). The coating solution is coated on suitable substrates (e.g. copper foil) with the aid of a plate spinner rotating at 78 rpm (revolutions per minute). After spinning for 5 minutes, the coating is dried with a 250-watt infrared heater mounted 15.0 centimeters above the center of the coated substrate. The sensitized substrate is then placed in a forced air oven at 66°C for 15 minutes to complete drying. Following exposure, the coating is developed in 0.25 N (normal) potassium hydroxide, trisodium phosphate, disodium phosphate, or triethanolamine for 1.5 minutes at 21.1°C. Note that if the alkali resistant resin is omitted in the preparation, layers about 150 micrometers thick are obtained. More recently Christensen[87] has learned that polyvinyl ethers, particularly polyvinyl methylether, also form superior photoresists with excellent resolution when used in Shipley's photoresist formula as an alkali-resistant resin. Then, Christensen and Isaacson[88] describe using substituted acrylamide in the preparation. The photoresists whose formulae are thusly described have been successfully employed in producing printing plates, forming resists for metal plating and for etching of metal or ceramics as in chemical milling or in the manufacture of printed circuit boards, and preparing holographic gratings and surface holograms.

A description of the preparation of holographic diffraction gratings in Shipley AZ 1350 photoresist is given by Grime.[89] These diffraction gratings are found to be superior to ruled diffraction gratings regarding scattered light and ghosts attributed to ruling errors. The simplest method to produce the holographic grating is to expose the positive photoresist on suitable substrate to two overlapping beams of collimated, monochromatic, spatially coherent light with a finite interbeam angle. Usually, the continuous wave argon ion laser operated at wavelength of 457.9 nanometers or a 75-milliwatt helium cadmium laser at 441.6 nanometers are used. The grating in

---

[87] Carl W. Christensen, "Light-Sensitive Naphthoquinone Diazide Composition Containing A Polyvinyl Ether," U.S. Patent 3,634,082, 11 January 1972.

[88] C. W. Christensen and C.M. Issacson, "Light Sensitive Quinone Diazide Composition With N-3-Oxohydrocarbon Substituted Acrylaminde," U.S. Patent 3,900,325, 19 August 1975.

[89] G.W. Grime, "Holographic Diffraction Gratings Recorded In Photoresist," in R.J. Cox (Ed.), *Non-Silver Photographic Processes,* New York, Academic Press, 1975 pp. 275-85.

positive photoresist, developed and dried, is given a highly reflecting, aluminum coating by evaporative methods in a vacuum.

An interesting application of holographic recording in Shipley's AZ 1350 photoresist or similar coating on a Mylar tape substrate is seen in the RCA holographic moving map display. Recording of three color separated, focused image or image plane, surface holograms that are angularly indexed enables the reconstruction of full color maps using three tungsten-halogen lamps equipped with either a red, green, or blue broad-band filter. Further the recording in the photoresist may be electroplated with approximately 50 to 75 micrometers of nickel that in turn becomes an embossing master upon stripping away the photoresist layer. The nickel master can then be used to emboss the full color holograms in heated clear vinyl plastic, or other plastics such as cellulose triacetate and polycarbonate, at rapid speeds. Stein[90] has published a review of the developments, and further treatment of the subject is given by Hannan et al.[91] Finally, evaluation of Shipley's AZ-1350-H photoresist has been carried out by Bartolini[92], and of Shipley's AZ-1350-J photoresist, by Norman and Singh.[93]

KODAK PHOTORESISTS AND OTHERS. The family of Kodak photoresists includes essentially five subfamilies of negative resists (i.e. Kodak Photo Resists (KPR), Kodak Ortho Resist (KOR), Kodak Metal-Etch Resist (KMER), Kodak Thin Film Resist (KTFR), and Kodak Micro Resists) and one subfamily of positive resist (i.e. Kodak Autopositive Resist, Type 3 (KAR3)). Bartolini[94] points out a difficulty in using negative photoresists such as Kodak KPR, KOR, KMER, KTFR, and the Micro Resists in preparing surface relief holograms. A conflict arises in the exposure needed to produce the best surface relief hologram and in the exposure needed to fix the photoresist firmly to the substrate so that the image does not become detached during development. Here one must know that with most negative-working photoresists the emulsion next to the substrate is the last to photolyze when the actinic light enters the emulsion at the emulsion-air interface. Until photolysis occurs at the emulsion-substrate interface, the resist material will simply dissolve in the developer even though it was in an exposed area of the plate. Possibly then the negative resist may be exposed through the glass or film substrate side so that the photoresist next to the substrate photolyzes first. Perhaps in this way the exposures needed to fix the resist material to the substrate and to produce the best surface relief in the hologram will coincide.

---

[90] Kenneth J. Stein, "Holographic Map Display Developed," *Aviation Week and Space Technology*, 22 April 1974 pp. 50-51.

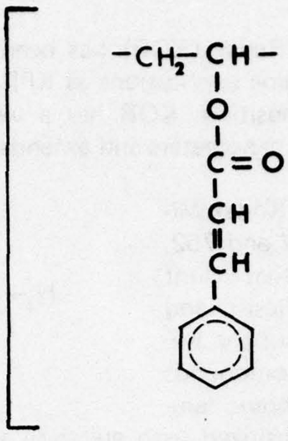
[91] W.J. Hannan, et al., *J. Soc. Motion Pict. Telev. Eng.*, Vol. 82, 1973 p. 905.

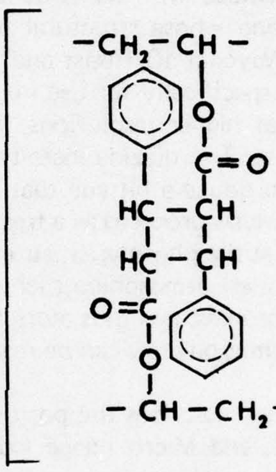
[92] R.A. Bartolini, "Characteristics of Relief Phase Holograms Recorded in Photoresists," *Applied Optics*, Vol. 13, January 1974, pp. 129-39.

[93] S.L. Norman and M.P. Singh, "Spectral Sensitivity and Linearity of Shipley AZ-1350J Photoresist," *Applied Optics*, Vol. 14, April 1975, pp. 818-820.

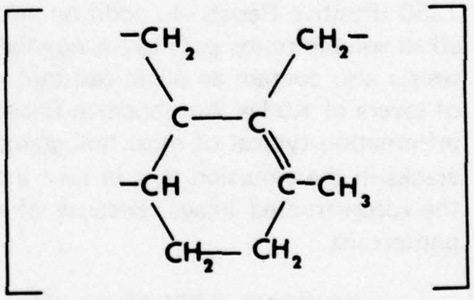
[94] R.A. Bartolini, "Characteristics of Relief Phase Holograms Recorded in Photoresists," *Applied Optics*, Vol.13, January 1974, pp. 131-2.

Clark[95] points out that the KPR photoresist was one of the first negative photoresists used in microelectronics. Here polyvinyl cinnamate with the formula illustrated top right is found to photo crosslink upon exposure to produce the higher molecular weight material illustrated just beneath it. A typical sensitizer is reported to be the azide compound 3-methyl-1, 3-diaza-1,9-benzanthrone, although Clark does say the polyvinyl cinnamate is intrinsically photosensitive. Production of consistently defined 2.5 micrometer lines can be obtained, but the resist in not very etch resistant. Etching the 2.5-micrometer lines leads to undercutting of the image and formation of pinholes. Thus, for microelectronic work, this resist has been generally replaced by one of the polyisoprene negative resist systems.





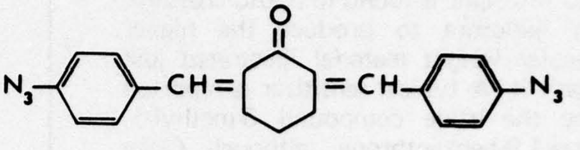
The first of the commercial polyisoprene photoresists is Kodak Metal Etch Resist (KMER) that is sensitized with 2,6-di-(4-azidobenzylidene)-4-methylcyclohexanone. Cis-polyisoprene has the structural formula shown on the right. Although the resist is high in inorganic impurities and ash content, it was found to have increased chemical resistance and adhesion. Thus, the tendency to form pinholes and to undercut is reduced. Kodak Thin Film Resist (KTFR) is another polyisoprene photoresist that is lower in organic impurities and ash content than KMER. Photoresist layers 0.8 micrometer thick have been obtained, and using vacuum contact printing techniques, it is possible to produce 2.5 micrometer lines and spaces in the KTFR layer.



---

[95] **Kenneth G. Clark, "Photoresist Techniques in Microelectronics," in R.J. Cox (Ed.)** ***Non-Silver Photographic Processes,*** **New York, Academic Press, 1975.**

Kodak Ortho Resist (KOR) has been used in electron-beam recording and may be used for the same applications as KPR, but no literature was found that describes its chemical composition. KOR has a very broad spectral sensitivity band that starts just below 250 nanometers and extends to 550 nanometers.



In addition to Kodak Micro Resists 747 and 752, Clark states that Hunt Waycoat IC Resist and Micro-Image Isopoly Resist consist of compounds of the polyisoprene family that are sensitized with an azide as, for example, the diazide 2, 6-di-(4-azidobenzal)-cyclohexanone whose structural formula is illustrated. The Kodak Micro Resist and the Hunt Waycoat IC Resist and perhaps the Micro-image Isopoly Resist as well were developed specifically for use in microelectronics that require optimal purity and etch resistance at higher resolutions. The diazide is very sensitive in the cis-polyisoprene photoresist. The diazide loses two molecules of nitrogen gas upon exposure to actinic light to produce a nitrene that crosslinks the polyisoprene through the double bond. The photolysis proceeds as a free radical process that is inhibited by atmospheric oxygen present at the photoresist, air interface. Exposure of photoresists of this family in a vacuum or inert atmosphere such as nitrogen prevents oxygen from interfering in the free radical process, and thus more favorable exposure times are realized. Images on the order of 2.5 micrometers can be readily obtained in the contact mode.

Again, Clark describes the positive working photoresists (e.g. Shipley AZ 1350-H, Hunt G-Line, and Micro Image Isofine) as those containing compounds prepared as formaldehyde condensation products (e.g. m-cresol formaldehyde novolaks, carboxymethyl ethers of formaldehyde, and phenol formaldehyde or acrylic monomers) sensitized with one of the diazo oxides as described in the subsection on Shipley AZ 1350 (Positive Resist). In addition to the diazo oxide sensitizer or sensitizers and the alkali soluble resins such as the novolaks, we have seen that the Shipley positive photoresists also contain an alkali resistant resin, such as polyvinyl methyl ether. Exposure of layers of Kodak Autopositive Resist, Type 3 (DAR3) to the high spatial frequency information typical of most holograms leads Bartolini[96] to report the development of cracks in the emulsion that in turn increase the quantity of noise due to scattering in the reconstructed image. Because of this, Bartolini prefers to use the Shipley 1350 photoresist.

HORIZONS RESEARCH INC. LHS7 PHOTORESIST. The Horizons LHS7 photoresist is a more recently developed, dry-working photoresist that can also be

---

[96] **R.A. Bartolini, "Characteristics of Relief Phase Holograms Recorded in Photoresists,"** ***Applied Optics*****, Vol.13, January 1974, p. 132.**

processed with liquid developers. Zech et al.[97] describe the photoresist as consisting of a highly reactive monomer in a thermoplastic binder, a spectral sensitizing dye, and a volatile halomethane activator. Exposure to actinic light produces changes both in the index of refraction and in the surface relief because of the formation of a polymer. The refractive index difference between monomer and polymer is reported to be fairly large, and the surface relief promoted by shrinkage in the layer upon polymerization of the monomer is sufficient to produce low efficiency holographic gratings. Still at this point, the refractive index difference is the dominant factor in hologram formation. After exposure, the photoresist may be processed for 90 seconds in a stream of rapidly moving air that is heated to 160°C. The volatile halomethane and monomer remaining in the unexposed regions is in this way removed from the layer, and these regions thereupon shrink to a level below that of the light-exposed regions. After heat processing, the surface relief is the dominant factor in hologram formation, and the refractive index differences produce only second order effects. Also, after heat processing, the photoresist can be further processed by solvent developing. It is assumed that the solvent developer then removes the remaining resist material, i.e. the thermoplastic binder, in the unexposed regions, thus producing the observed contrast enhancement. Solvent development is found to increase the spatial frequency response of the photoresist, but it also brings about a significant increase in light scattering. Hence, Zech did not pursue solvent processing, which is not needed for hologram formation. The remaining sensitizing dye is photobleached to the colorless leuco state.

No information was found on the chemistry of the materials used in Horizons LHS7 Photoresist. However, a study of known photopolymer processes may help to elucidate the nature of the materials used (i.e. Kosar[98]). For example, it's known that iodoform and carbon tetrabromide, examples of halomethanes, can be photolyzed in near UV light or in VIS light with the aid of a sensitizing dye to form the highly reactive free radicals. These iodine or bromine free radicals in turn react with different monomers (e.g. methacrylic acid or vinyl methyl ether) to produce a second highly reactive free radical that in turn reacts with a second monomer molecule to form still a third highly reactive dimer free radical. The addition of successive monomer molecules to the ever growing polymer free radical continues until either two free radicals combine to form a stable polymer or the polymerizing reaction is stopped through some other process, such as that promoted by atmospheric oxygen. Kosar reports a process described by Levinos and Mueller in which relief images are produced in monomer material on dye sensitized, silver halide gelatin emulsions. The dye upon exposure to light absorbs the energy and transfers the energy to silver halide crystallites such as silver bromide. A bromine free radical is produced, the same as can be pro-

---

[97] R.G. Zech, J.C. Dwyer, H. Fichter, and M. Lewis, "Heat-Processed Photoresist for Holographic Data Storage Applications," *Applied Optics*, Vol. 12, December 1973, pp. 2822-7. Also Final Technical Report No. F30602-74-C-0030, Rome Air Development Center, Griffiss AFB, New York, July 1974, pp. 28-46.

[98] Jaromir Kosar, *Light-Sensitive Systems: Chemistry and Application of Non-Silver Halide Photographic Processes*, New York, John Wiley and Sons, 1965, pp. 180-7, 364-8.

duced from carbon tetrabromide, that in turn initiates the polymerization of a highly reactive monomer such as the vinyl monomers. The polymerization of vinyl monomers then is promoted by bromine free radicals or atoms at the silver halide surface, building up a relief image in polymer corresponding to the incident radiation at the surface.

Zech et al. conclude that the Horizons LHS7 photoresist is well suited for use in many holographic data storage applications. It provides holograms whose reconstruction parameters compare very well to high quality holographic recording materials, such as Kodak 649F plates, at the lower spatial frequencies.

IRON OXIDE. Colburn et al.[99] find iron oxide holograms attractive because iron oxide is known to be impervious to adverse environmental conditions of temperature and relative humidity. The oxide forms thin phase holograms on glass substrates. Iron oxide thin films are prepared on glass substrates by the thermal decomposition of iron pentacarbonyl ($Fe(CO)_5$) vapor in oxygen in a specially heated decomposition chamber. Iron oxide films of 90 to 400 nanometers thick are obtained. Since iron oxide is not photosensitive, the thin films are coated next with a layer of a positive photoresist, perhaps Shipley AZ 1350 positive photoresist. A spinner is used to produce uniform layers. The coated iron oxide plate is ovendried in the air for 30 minutes at 100°C to remove residual solvent and water. After exposure, such as to an interference pattern of two overlapping collimated and coherent laser beams, the photoresist is developed and ovendried a second time. The iron oxide layer may then be etched with dilute hydrochloric acid with a concentration sufficient to give etching times of from 10 to 20 seconds. Colburn reports a typical etchant concentration as 10 Molar HCL. After etching the iron oxide hologram is rinsed in distilled water, the remaining photoresist is removed with appropriate solvent, and the hologram plate is air-dried. Exposing the photoresist, developing the photoresist, and etching the iron oxide layer are critical processing steps.

As expected Colburn et al. found the iron oxide holograms were not affected by changes in temperature and percent relative humidity. The diffraction efficiency is found to remain nearly constant for all values of temperature and percent relative humidity studied.

## HARDENED DICHROMATED GELATIN

BACKGROUND. The distinguishing feature of hardened gelatin is that unlike unhardened gelatin thin layers will not dissolve in water, although they will swell to three or four times their dry thickness. Pouradier and Burness[100] treat hardening of

---

[99] W.S. Colburn, R.G. Zech, and L.M. Ralston, *Holographic Optical Elements*, Final Technical Report, Wright Patterson Air Force Base, Ohio, January 1973, p. 109.

[100] J. Pouradier, and D.M. Burness, "The Hardening of Gelatins and Emulsions," in T.H. James (Ed.) *The Theory of The Photographic Process*, New York, Macmillan Co., 1966, pp. 54-60.

gelatin and emulsions and point out, first, that photographic emulsions are hardened during manufacture to protect against the effects of high temperatures and humidities. Second, the emulsions may be hardened during processing to keep the wet gelatin firm and undisturbed. Third, the gelatin may be further hardened through photochemical processes that produce inorganic or organic hardeners as photolysis products. Inorganic hardeners include chromium salts, aluminum salts, and potassium and ammonium alums. The chromic oxide formed during the photolysis of ammonium or potassium dichromate in gelatin layers is believed to crosslink two gelatin protein chains through coordination with carboxyl groups on the chains. Organic hardeners include the chemical families of aldehydes, ketones, acids, and others that augment hardening of the gelatin through formation of strong hydrogen bonds, such as afforded by alcohol, phenols, or amines. Many of the organic hardeners promote hardening of gelatin by crosslinking two amine groups on the lysine amino acid side chains located at different points along the gelatin protein chain. Chang[101] describes Jolley's picture of the microstructure of photographic gelatin. Gelatin is a long-chain polymer that is made up of a polar and nonpolar parts. These two structural features contribute to the physical properties of gelatin films. The nonpolar parts may be induced to form a triple stranded helix from three different chains or molecules by chilling layers of their solution and allowing the layers to dry below 35°C. The triple stranded helix, the collagen helix, is crystalline in nature, and the helix orientates itself parallel to the plane of the substrate it is on. The polar sections of the gelatin protein chain do not appear to associate with each other unless the chemical crosslinks are formed through the hardening agents described above. Should layers of gelatin solutions be allowed to dry above 45°C, the gelatin layers formed are almost amorphous and are without formation of the collagen helix. Chang states that upon dehydration the amorphous films (by placing them in dry alcohol) tend to crack more readily than the crystalline films. For further interesting information on the crosslinking of gelatin, the reader is referred to a subsection of that description in a book edited by Cox.[102] It would appear from the above description that gelatin is susceptible to crosslinking in at least two different sites in the long polar protein chain and that the nonpolar portion of the protein chain may be arranged in the crystalline collagen helix or in the amorphous dissociated form, depending upon the thermal history of the material.

The mechanism by which hologram formation occurs in hardened dichromated gelatin can now be traced. Chang,[103] Zech,[104] Meyerhofer[105] and finally Close et

---

[101] Milton Chang, "Dichromated Gelatin of Improved Optical Quality," *Applied Optics*, Vol. 10, November 1971, pp. 2550-1.

[102] R.J. Cox (Ed.), *Photographic Gelatin*, New York, Academic Press, 1972, pp. 99-156.

[103] Ibid. P. 2551

[104] R.G. Zech, *Data Storage in Volume Holograms,* Doctoral Dissertation, University of Michigan, 1974, p.219.

[105] Dietrich Meyerhofer, "Phase Holograms in Dichromated Gelatin," *RCA Review*, Vol.33 March 1972, p. 119.

al.[106] give detailed descriptions of preparations used to make the hardened dichromated gelatin plate either from commercial silver halide plates or from prepared coating solutions. Zech gives a preparation for making the photosensitive layer from coating solutions, and Close treats preparation of a red sensitive dye-sensitized layer using commecial silver halide plates. The commercial plates and the prepared gelatin plates already contain hardened gelatin. These plates are further hardened in fixer with hardener. Following washing and drying, the gelatin layer is sensitized with approximately 5 percent ammonium dichromate solution with or without ammonium nitrate and with a dye sensitizer, such as methylene green. Following drying, the hardened dichromated gelatin plate is exposed to an interference pattern of two overlapping, collimated, coherent light beams. The exposed plate is then washed to remove the dichromate and any other soluble compounds and dehydrated in a series of isopropyl alcohol baths. The strain produced through rapid dehydration of the gelatin layer in the alcohol forms cracks or tears in the lesser hardened, unexposed regions of the layer. Further, a complex compound is formed consisting of the isopropyl alcohol coordinated with the chromium (III) ion at the gelatin corsslinked sites as reported by Meyerhofer.[107] The strain-induced cracks are treated in some detail by Curran and Shankoff.[108] The air, gelatin interfaces denoted as cracks in the gelatin are very efficient at redirecting light into the first order. The isopropyl alcohol chromium III complex entity also adds to the phase change. Consequently, diffraction efficiencies in excess of 90 percent for a plane wave gratings, and a signal-to-noise ratio of 27 decibels are reported by Zech. The holograms and holographic optical elements recorded on hardened dichromated gelatin have remarkable brightness and resolution.

Hardened dichromated gelatin have typical exposure requirements of about 100 millijoules per square centimeter and are considered to be among the less sensitive holographic recording materials. Underexposed holograms exhibit a milky-white opacity that seriously degrades the reconstructed image when it occurs. Chang[109] points out that the amorphous form of the gelatin produces the milky-white opacity more readily than the crystalline form and that the drying temperature for pretreating gelatin film is important. He proposes using near room terperatures as being optimal for pretreating gelatin layers.

---

[106] D.H. Close and A. Graube, *Holographic Lens For Pilot's Head-Up Display*, Hughes Research Laboratory, Malibu, California, N-62269-73-C-0388, August 1974, NTIS: AD-787 605, P. 93.

[107] Dietrich Meyerhofer, "Phase Holograms in Dichromated Gelatin," *RCA Review*, Vol. 33, March 1972, p. 118.

[108] R.K. Curran and T.A. Shankoff, "The Mechanism of Hologram Formation in Dichromated Gelatin," *Applied Optics*, Vol. 9, July 1970, p. 1651-57.

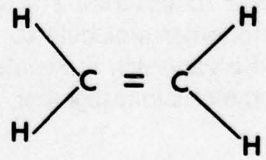
[109] Milton Chang, "Dichromated Gelatin of Improved Optical Quality," *Applied Optics*, Vol. 10, November 1971, pp. 2550-1.

The spectral sensitivity of ammonium dichromated gelatin layers extends from 350 to 520 nanometers. Close et al.[110] have examined 120 dyes for dye sensitizing the dichromated gelatin in the red region of the spectrum. They learned that a red, absorbing, photoreducible dye incorporated in the dichromated gelatin layer promotes the photoreduction of the dichromated ion to the chromium (III) ion needed to cross-link the gelatin protein chains. Their survey revealed that the thiazine and triphenylmethane dyes are the two classes of dyes best suited to dye sensitize dichromated gelatin in the red spectral region. They optimized a coating formulation using high concentrations of ammonium dichromate and ammonium nitrate and using methylene green dye. In addition to the sensitization of dichromated gelatin in the manner of Close, Akagi[111] reports sensitization of the gelatin in the red spectral region with methylene blue to which is added an acid amide (e.g. acetamide, N,N-dimethylformamide and N-methyl-2-pyrrolidone). Here the acid amide is the source of electrons for the reduction of the methylene blue. Akagi reports using the 632.8 nanometer line of a helium neon laser to expose his red-sensitive, dichromated gelatin for the production cf plane wave gratings.

Close et al. developed a red-sensitive, hardened dichromated gelatin to prepare a 406.4 millimeter (16-inch) diameter holographic optical lens. The lens is to be used for a pilot's head-up display. The basic system parameters are a field of view of 25°, an exit pupil size of 76.2 millimeters (3 inches) high by 127.0 millimeters (5 inches) wide, and an eye relief of 635.0 millimeters (25 inches). A high optical efficiency of 80 percent with low scattering losses is expected for the holographic optical lens.

## PHOTOPOLYMERS

BACKGROUND. Polymerization is a chemical process by which small molecules are combined to make very large molecules. The small molecules are called monomers in the initial state, and the very large molecules are called polymers. Polymerization is one of the most important reactions of alkenes, which are a family of monomers characterized by a single double bond in each molecule denoting the absence of a pair of hydrogen atoms. The simplest alkene is ethylene, which is a gas under standard conditions of temperature and pressure. Unlike the saturated hydrocarbon ethane, ethylene has one pair fewer atoms and, therefore, a double bond in its molecule denoted thusly:

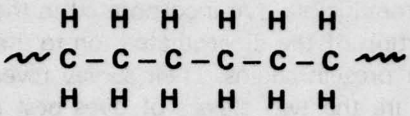


---

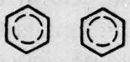
[110] D.H. Close and A. Graube, ***Holographic Lens For Pilot's Head-Up Display,*** **Hughes Research Laboratory, Malibu, California, N-6229-73-0388, August 1974, NTIS: AD-787 605, pp. 16, 80.**

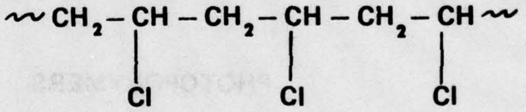
[111] **Motoo Akagi, "Spectral Sensitization of Dichromated Gelatin,"** ***Photographic Science and Engineering,*** **May/June 1974, pp. 248-250.**

When ethylene is heated under pressure with oxygen, a very long chain polymer is formed that is made up of many ethylene units, thus: or $(-CH_2-CH_2-)n$ in which $n > 1000$. The polymer formed is polyethylene and is familiar as a plastic material used in the manufacture of flexible bottles and packaging films. There are many substituted ethylenes that polymerize either more or less readily to produce plastics with widely differing physical properties. For example, there is vinyl chloride, $CH_2 = CHCL$; styrene, $CH = CH_2$; vinyl acetate, $CH_2 = CHO\underset{\underset{O}{\|}}{C}- CH_3$ from which we get polyvinyl alcohol as well as polyvinyl acetate; methyl methacrylate, $CH_2 = \underset{CH_3}{C} - \overset{/\!/ O}{C} - OCH_3$; and stilbene $CH = CH$. Polymerization of these substituted ethylenes produces polymers whose structure is like that of polyethylene but with the substituent groups attached more or less at regular intervals in the polymer chain. For example, polyvinyl chloride looks like the illustration on the right or like the illustration just below.

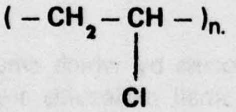


$$\sim C(H)(H) - C(H)(H) - C(H)(H) - C(H)(H) - C(H)(H) - C(H)(H) \sim$$





$$\sim CH_2 - \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH} \sim$$

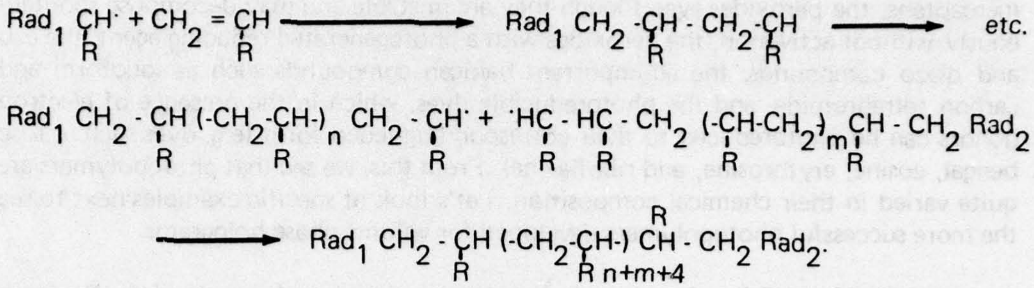


$$( - CH_2 - \underset{Cl}{CH} - )_n.$$

Polymerization as such requires the presence of a small amount of a chemical that can form a free radical known by chemists to initiate the polymerization process. A common free radical initiator is a member of the chemical family of peroxides. When a peroxide breaks down, it forms radicals that readily add to the molecules of substituted ethylenes to generate still another free radical. The second free radical adds to a second monomer molecule to form still a larger free radical. The chain thus grows to produce the very high molecular weight polymer that is finally formed when two very large free radicals join together. Thus, we have

$$\text{Peroxide} \xrightarrow[\text{dissociates}]{} Rad_1 + Rad_2$$

$$Rad_1 + CH_2 = \underset{R}{CH} \longrightarrow Rad_1\, CH_2 - \underset{R}{CH}\cdot$$

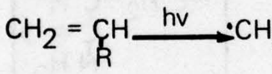


$$\mathrm{Rad_1\,\underset{R}{CH^{\cdot}} + CH_2{=}\underset{R}{CH} \longrightarrow Rad_1\,CH_2\text{-}\underset{R}{CH}\text{-}CH_2\text{-}\underset{R}{CH} \longrightarrow}\ \text{etc.}$$

$$\mathrm{Rad_1\,CH_2\text{-}\underset{R}{CH}(\text{-}CH_2\text{-}\underset{R}{CH}\text{-})_n\,CH_2\text{-}\underset{R}{CH^{\cdot}} + {}^{\cdot}\underset{R}{HC}\text{-}\underset{R}{HC}\text{-}CH_2\,(\text{-}\underset{R}{CH}\text{-}CH_2\text{-})_m\,\underset{R}{CH}\text{-}CH_2\,Rad_2}$$

$$\mathrm{\longrightarrow Rad_1\,CH_2\text{-}\underset{R}{CH}(\text{-}CH_2\text{-}\underset{R}{CH}\text{-})_{n+m+4}\,\overset{R}{CH}\text{-}CH_2\,Rad_2.}$$

Occasionally a monomer itself can be excited directly to form a free radical that initiates the polymerization process. However, compounds that more readily generate free radicals are added to the monomer solution to initiate the polymerization. Radicals may be generated through the pyrolytic decomposition of the initiating compound, through electron transfer processes, or through photolytic processes. Of course, it is the photolytically produced radicals that give rise to photopolymerization processes that are of direct interest here.

Kosar[112] points out that the energy needed to promote bond rupture in most covalent bonds corresponds to light with the wave length of 300 to 590 nanometers. Thus, a substituted vinyl compound will form a free radical upon exposure to actinic light,  $\mathrm{CH_2 = \underset{R}{CH} \xrightarrow{hv} {}^{\cdot}CH_2 - \underset{R}{CH^{\cdot}}}$. The radical thus formed produces polymerization of the monomer in the surrounding area. Again however, a radical photogenerating compound other than the monomer is added to the monomer solution to photoinitiate the polymerization. Such photoinitiators may also form free radicals at wave lengths greater than 590 nanometers or be dye-sensitized to do so. This will be discussed later.

There are many examples of photoinitiators, those initiators that promote the the photopolymerization process. Kosar treats seven different families of initiators known to bring about photopolymerization. In the family of carbonyl compounds, he points out that benzoin, $C_6H_5{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_5$, and its derivatives in particular are the subject of a number of patents issued to the DuPont Company. Other families of photoinitiators are the organic sulfur compounds, including the disulfides and

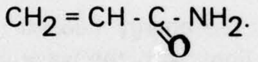
---

[112] Jaromir Kosar, ***Light-Sensitive Systems: Chemistry and Applications of Non-Silver Halide Photographic Processes,*** **New York, John Wiley and Sons, Inc., 1965, p. 159.**

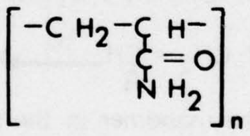
mercaptans, the peroxides even though they are unstable and may decompose spontaneously without activation, the peroxides with a photogenerated reducing agent, the azo and diazo compounds, the all-important halogen compounds such as iodoform and carbon tetrabromide, and the photoreducible dyes, which in the presence of electron donors can be photoreduced to their corresponding leuco form (e.g. dyes such as rose bengal, eosine, erythrosine, and riboflavine). From this, we see that photopolymers are quite varied in their chemical composition. Let's look at specific examples next to see the more successful photopolymers developed for volume phase holograms.

HUGHES – NRC. Certain photopolymers developed by Hughes Research Laboratories may be obtained commercially from the Newport Research Corporation, (NRC) who has exclusive rights from Hughes to manufacture and market them for use in holography. The literature describing the Hughes-NRC photopolymers is presented here as set forth by personnel of Hughes Research Laboratories.

The literature suggests that the Hughes-NRC photopolymers consist of aqueous solutions of acrylamide, one of a number of dye sensitizers (e.g. methylene blue), and an initiator or catalyst consisting of a derivative of the benzenesulfinate ion or the ion itself. The acrylamide monomer is another substituted vinyl monomer with the following structural formula:



$$CH_2 = CH - \underset{\substack{\| \\ O}}{C} - NH_2 .$$



$$\left[-CH_2-\underset{\substack{| \\ C=O \\ | \\ NH_2}}{CH}-\right]_n$$

Upon polymerizing, the acrylamide monomer becomes like that shown on the right in which 'n' is a very large number. Margerum et al.[113] describe the photoinitiator as a photoredox polymerization initiation system in which excited methylene blue in the singlet state is found to form an excited triplet state. It appears that it is the triplet state dye molecules that react with the sulfinate ions to produce the sulfonyl free radicals denoted $RSO_2\cdot$ and dye free radicals denoted $D\cdot$. Further, it appears that it is the sulfonyl radicals that react with the acrylamide monomer in promoting the photopolymerization process. Although Margerum does not propose that dye radicals themselves initiate photopolymerization of the acrylamide monomers, it is not clear why this would not happen if indeed methylene blue free radicals are formed. However, he does show the formation of dye molecule polymer entity as an end step to the polymerization process, and he states that both the sulfonyl group and the dye molecules are chemically incorporated in the polyacrylamide polymer.

---

[113] J.D. Margerum, A.M. Tenorio, C.T. Petrusis, and M.J. Little, "Studies on the Mechanism of Dye-Sensitized Photopolymerization Initiation," *Polymer Preprints For the 160th American Chemical Society Meeting*, Chicago, Ill., 15 September, 1970.

In preparing the photopolymer for recording holograms, the monomer and dye sensitized photoinitiator are mixed just before use. Since the mixed monomer and photoinitiator are not stable for more than 1 hour, small quantities are mixed using syringes to measure the volumes easily. A few drops of the mixed polymer solution are enclosed between two glass cover slides for the holographic exposure. If no spacers are used, a film thickness between 5 and 15 micrometers is obtained. The best results have been obtained with films in this thickness range. Cover slides up to 82.6 by 101.6 millimeters (3.25 by 4 inches) have been successfully used. Exposure is accomplished in the visible spectral region and is dependent upon the dye sensitizer used. A uniform pre-exposure may be used during which very little polymer is formed and which according to Jenney[114] reduces the requried exposure to form a hologram by using up dissolved oxygen and any other such polymerization inhibitors. Further, Tomlinson et al.[115] point out that any polymer formed increases the viscosity of the photosensitive material and aids in forming stable images. An ultraviolet sensitive fixing agent is also included in the photopolymer whose photolysis products chemically reduce the sensitizing dye to its colorless leuco form. Thus, a simple post exposure to an ultraviolet source readily fixes the photopolymer.

Brault et al.[116] have prepared scanning electron microscope views of the surface of a photopolymer containing a plane wave grating. These views demonstrate that the image storage mechanism includes a thickness modulation. The thickness modulation is believed to be the dominant contributor to the diffraction with only a small contribution from the index of refraction differences in the bulk material. Since the diffraction is promoted by a surface modulation in the photopolymer, the diffraction efficiency approaches a limit near 30 percent.

DUPONT COMPANY. The DuPont photopolymer material is reported by MacDonald and Hill[117] to consist of the acrylate monomers that are of the substituted vinyl type with an absorption range in the near ultraviolet (330 to 360 nanometers), a photoinitiator that extends the photosensitivity into the visible region (approximately 550 nanometers), and a cellulose polymer binder that forms a matrix to hold the liquid monomer. Previously, the emulsion was coated on film and pressure-laminated to glass plates. Now, the experimental holographic photopolymer is available as a

---

[114] J.A. Jenney, "Holographic Recording With Photopolymers," *J. Opt. Soc. Am.* Vol. 60, 1970, p. 1155.

[115] W.J. Tomlinson, E.A. Clandross, H.P. Weber, and G.D. Aumille, "Multicomponent Photopolymer Systems For Volume Phase Holograms and Grating Devices," *Applied Optics,* Vol. 15, No. 2, February 1976, p. 540.

[116] R.G. Brault, J.A. Jenney, J.D. Margerum, L.T. Miller, and J.B. Rust, "Rapid Access Photopolymerization Imaging," *Proc. of SPSE Seminar on Applications of Photopolymers,* 3 April, 1970, pp. 113-132.

[117] R.I. MacDonald and K.O. Hill, "Evaluation of A New Photopolymer Hologram Recording Medium," Communications Research Center, Ottawa, Canada, September 1973, NTIS Report No. N-73-32395.

liquid photopolymer solution in a methylene chloride, methanol solvent ready for coating on film or glass. The photopolymer solution has a 3-month storage life if kept in a refrigerator. Although no information is given on the photoinitiator, we have seen that DuPont has a number of patents treating benzoin and its derivatives such as benzoin methyl ether. This suggests that a dye-sensitized benzoin derivative may be used as the photoinitiator. A post exposure serves to bleach the dye sensitizer, which has a peak absorption at 475.0 nanometers.

The mechanism of hologram formation in the DuPont photopolymer material involves three steps as explained by Colburn and Haines.[118] First, exposure to actinic radiation promotes polymerization of monomer in the light struck regions. Should the exposing radiation be an interference pattern produced by the overlapping beams of coherent light, monomer concentration gradients arise across the interface between the light struck regions and the unexposed regions. This gradient promotes the second step namely the diffusion from the monomer-rich unexposed regions to the monomer-depleted, polymer-rich exposed regions. If the light intensity is low (2 milliwatts per square centimeter), then, as Booth[119] points out, the diffusion rate of the monomer does not exceed the polymerization rate, and the diffraction efficiency can be monitored during exposure using the 632.8-nanometer line of the HeNe laser to which the sensitized monomer is insensitive to. At light intensities 2 milliwatts per square centimeter, the diffusion rate of the monomer is less than the polymerization rate, and the diffraction efficiency first increases, then decreases as monomer begins to diffuse into the exposed regions lowering the refractive index modulation. The rate of the decrease in diffraction efficiency depends upon the diffusion distance, which should be one-half the reciprocal of the recorded spatial frequency. At spatial frequencies of 200 millimeters$^{-1}$, the diffusion time is approximately 1.5 seconds. Colburn and Haines point out that there is no variation in surface relief seen at the spatial frequencies used in hologram formation. Therefore, hologram formation is believed to involve variations in density and hence in refractive indices in the final photopolymer product. The third step is a post exposure, which is a uniform exposure, that photobleaches the dye sensitizer and also completes polymerization of all monomer material, thus fixing the photopolymer as a volume phase hologram. Diffraction efficiencies approaching 100 percent are reported.

It is interesting to note that the inhibition to polymer formation produced by the presence of oxygen in the polymer layer may be reduced and perhaps even eliminated by exposing the photopolymer layer in a nitrogen atmosphere. The oxygen present in the layer reacts with any free radicals formed during the exposure reducing their number. Exposures on the order of 10 to 40 millijoules per square centimeter in

---

[118] W.S. Colburn and K.A. Haines, "Volume Hologram Formation in Photopolymer Materials," *Applied Optics*, Vol. 10, No. 7, July 1971, p. 1636.

[119] B.L. Booth, "Photopolymer Material For Holography," *Applied Optics*, Vol. 14, No.3, March 1975, pp. 593-601.

the air are reduced to 1 to 4 millijoules per square centimeter in nitrogen or other oxygen-free atmospheres.

BELL LABORATORIES. Tomlinson et al.[120] describe multicomponent photopolymer materials for the production of volume phase holograms. Unlike the previous photopolymer materials that contain singular monomer or a mixture of similar monomer materials, two or more monomers are selected so that they have substantially different photochemical reactive rates and refractive indices following their polymerization. During the exposure to the interference fringes produced by overlapping coherent beams of light, the regions with the higher light intensity is polymerized to a greater degree than the adjacent regions with lower intensity light. The higher reactive monomer will be preferentially polymerized. This produces a concentration gradient in the higher reactive monomer that promotes its diffusion into the polymer rich region. As the polymerization proceeds, the polymer rich region increases in concentration, squeezing out the lower reactive monomer into the region of lower intensity light. Thus, the lower light intensity regions will contain predominantly the lower reactive monomer, and the higher light intensity regions will contain polymer formed from the higher reactive monomer. After completing polymerization of both monomers then, one is left with a modulation in the chemical composition of two materials with different molecular polarizabilities and therefore different refractive indices. Tomlinson reports that the modulation in refractive indices resulting from the modulation in chemical composition tends to be larger than the modulation in refractive indices observed in the previous photopolymer materials that contain a singular monomer or a mixture of similar monomer materials.

Essentially, two different multicomponent photopolymer materials were described that gave stable holograms. The first of these contained the acrylate monomer, cyclohexyl methacrylate as the high reactive monomer, vinylcarbazole as the low reactive monomer, and benzoin methyl ether as the photoinitiator. A reactivity ratio of 40:1 under relevant conditions is reported. The refractive indices of the respective polymers are 1.505 for the polyacrylate and 1.690 for the polyvinylcarbozole. Exposures at 325 nanometers were approximately 750 millijoules per square centimeter, which excludes a necessary pre-exposure to obtain maximum index of refraction change. Gratings prepared as thin as 5 micrometers produced first order diffractions in the reflective mode. This denotes that the gratings produced are true volume phase gratings with little or no surface modulation. The second multicomponent photopolymer material contained an acrylate monomer, butyl methacrylate; a bifunctional monomer, ethylene glycol dimethacrylate, which serves as a crosslinking monomer; an inert component that has a zero polymerization rate, namely 1-phenylnaphthalene; and the photoinitiator benzoin methyl ether. The refractive index of the 1-phenylnaphthalene is 1.666 and for the pure copolymers is approximately 1.500. Exposures at 325 and 364 nanometers are in the range 0.9 to 2.7 joules per square centimeter. Both a pre-exposure and a post exposure to an actinic source are essential to obtaining the maximum index modulation.

---

[120] W.J. Tomlinson, E.A. Chandross, H.P. Weber, and G.D. Aumiller, "Multicomponent Photopolymer Systems For Volume Phase Holograms and Grating Devices," *Applied Optics*, Vol.15, No. 2, February 1976, pp. 34-541.

One application of the multicomponent photopolymers has been in fabricating fiber grating filters. The grating filters over 5 millimeters long have been prepared in hollow silica fibers with an inside diameter of 80 micrometers and an outside diameter of 600 micrometers. To minimize shrinkage of the photopolymer material in such constant volume cavities, the material composition ofr the grating filters must be carefully selected even though the refractive indices differences may be somewhat reduced. This led to the selection of a variation of the second multicomponent photopolymer material in which the total monomer fraction was only 17 percent, and 25 percent of the monomer was bifunctional. Stable gratings were prepared with these materials without cracking or formating voids, but the refractive index differences was lower. Tomlinson reports that by using high concentrations of inert components and monomers with low shrinkage,grating materials could be prepared whose surface attraction to the walls of the cavity offset shrinkage.

## PHOTOCHROMIC MATERIALS

BACKGROUND. A good introduction to photochromism and photochromic materials is found in Kosar.[121] With photochromic materials the reverse color change of compounds with actinic light is associated with a change in the molecular structure. Hence, photochromism is a photochemical process that obeys the Grothus Draper Law. Whereas it is actinic radiation that produces the initial color change in the material, it is a second photolytic process, produced by light usually at a different wave length, a thermal process, or a combination of the two, that produces the reverse color change. If the photochromic material is arranged so that both the initial photolytic process and the reverse color process occur simultaneously, which is generally the case, then the rates at which these processes proceed determine the optical density obtained. In fact, Slack states that all three competing reactions (namely, the forward or initial photolytic reaction, the reverse thermal reaction, and the reverse photolytic reaction) can occur simultaneously.[122] Examination of three possible cases follows.

For the process, $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$ in which A, a photosensitive compound, is photolyzed to compound B at rate $k_1$ and B is thermally reversed to A at rate $k_2$, and further if the actinic light produces a zero-order reaction while heat produces the reverse process that is proportional to the concentration of B formed, then a steady state will be obtained in which the two rates are equal. This is described by

$$\frac{d(B)}{dt} = k_1 I - k_2(B)$$

in which I equals the intensity of the light, and (B) equals concentration of the pho-

---

[121] Jaromir Kosar, *Light-Sensitive Systems,* New York, John Wiley and Sons, Inc., 1965, pp. 380-386.

[122] C.T. Slack, "Calculations of the Response Curve of a Solid Photochromic Film," *Optica Acta,* Vol. 17, No. 7, July 1970, pp. 547-558.

tolysis product, B. At steady state when $\frac{d(B)}{dt} = 0$, one finds $k_1 I = k_2(B)$ and $(B) = \frac{k_1}{k_2} I$.

From this, one concludes that the concentration of B (denoted (B)) tends to increase with increasing light intensity. In an isotropic medium, the absorption will be dependent upon (B); therefore, the optical density will also be dependent upon (B). Also, factors that change the rate constants $k_1$ and $k_2$ (e.g. temperature) will tend to alter the final optical density.

For the case in which the reverse process (i.e. $B \xrightarrow{k_2} A$) is a photoreverse process and in which there are no thermal effects, then supposedly $\frac{d(B)}{dt} = k_1 I_1 - k_2 I_2$ and at steady state $k_1 I_1 = k_2 I_2$. This implies that the rate constant $k_1$ is dependent upon the intensity of the light $I_1$ used to irradiate A, that the rate constant $k_2$ is dependent upon the intensity of the light $I_2$ used to irradiate B, and that $I_1 \gg I_2$ for an image to be observed with good optical density.

For the case in which the reverse process (i.e. $B \xrightarrow{k} A$ occurs as both a thermal-reversed and a photo-reversed process, the following is derived:

$A \xrightarrow{k_1} B$ zero order, photolytic process

$B \xrightarrow{k_2} A$ first order, thermally reversed process

$B \xrightarrow{k_3} A$ zero order, photolytic process

Then $\frac{d(B)}{dt} = k_1 I_1 - k_2(B) - k_3 I_2$ in which $I_1$ equals the intensity of light at wavelength $\lambda_1$, $I_2$ equals the intensity of light at wavelenght $\lambda_2$, and (B) equals the concentration of compound B. At steady state, $(B) = \frac{k_1 I_1 - k_3 I_2}{k_2}$. Again this favors $I_1 \gg I_2$ or the case in which $I_2 \rightarrow 0$ for improved contrast or high optical density.

Generally then, reversible photochromic materials must remain illuminated by the initial photolyzing light at wavelength $\lambda_1$ to maintain an appreciable optical density in the image areas during readout. One obtains higher image contrast by maintaining the photochromic material at lower temperatures and by using light at wavelength $\lambda_2$ at lower intensities to read out with. Finally, light absorption is accompanied by singular molecular transitions in purely isotropic photochromic materials. Hence, resolutions of photochromic materials should not be limited by the material itself but should be light wavelength dependent, and the photosensitivity should be correspondingly low.

SILVER HALIDE GLASSES. Tsekhomskii and Tunimanova[123] describe photochromic glasses prepared on the basis of the silver halides. Usually the different halides are incorporated in a matrix of the silicate glasses as grains approximately 5 to 30 nanometers in diameter. Silver chloride photochromic glasses are typically transparent in the visible region, the absorption edge being located in the 350 to 400 nanometer spectral region. Incorporation of silver bromide in the glass displaces the absorption edge toward the red to 450 to 500 nanometers. Upon exposure to actinic light below the absorption edge, an additional absorption peak appears in the visible region at approximately 550 nanometers. The spectral band extends from the near ultraviolet to the near infrared spectral region. Exposure of the photochromic glass to light in this wide band absorption region in the visible produces the so-called photobleaching effect that, in addition to any thermally promoted reversal reaction, restores the photochromic material to its initial state. The rates of any thermal bleaching is dependent upon the composition of the photochromic glass and its temperature. Here Tsekhomskii and Tunimanova describe two different glasses, one with a halflife thermal decay rate of 5 seconds and the second with a decay rate of approximately 40 calendar days. Although no information is given on the composition of these two materials, perhaps the former material consists of a glass matrix with an appropriate halide addition or of a matrix that is inert to the photolytic halogen produced by the initial exposure. Those photochromic materials with sufficiently long decay times can be used to produce holograms using light either in the spectral region below the initial absorption edge or in the resulting absorption band across the visible spectral region. Hence, by using the broad band in the visible spectral region, it is possible to use the 647.l nanometer spectral line of the krypton ion laser to prepare the hologram.

A description of different properties treated by Tsekhomskii and Tunimanova in their article on photochromic glasses follows. The halide glasses are reported to have chemical stability greater than that of the Lippmann emulsions (e.g. Kodak 649F plates). The small halide grain size influences the resolving power and the low light sensitivity of these glasses. No change in the diffraction efficiency is seen for interbeam angles of 10° to 40° for the two interfering beams of coherent light, and this only falls to one-third of its maximum value at an interbeam angle of 70° for light at 632.8 nanometers. Here the minimal resolving power is in excess of 2,000 lines per millimeter. The low light sensitivity is approximately 5 orders of magnitude less than that of the photographic emulsions, there being no amplification by chemical development typical of silver halide photography. Still, it is possible to detect a holographic image for exposure time of $10^{-2}$ seconds and exposure times of approximately $10^{2}$ seconds are needed to produce a photographic density of 0.2. This demonstrates that the suitability of photochromic glasses is more for holography rather than for photography and also suggests that those properties are essential to the high dynamic range exhibited by these materials. The silver halide photochromic glasses have an extended

---

**[123] V.A. Tsekhomskii, and I.V. Tunimanova, "Photochromic Glasses," Translation From *Transactions of the 1st All-Union Conference on Non-Silver and Novel Photographic Processes,* Section IV, Kiev, Ukrainian SSR, 1972, pp. 113-119.**

linearity of diffraction efficiency region in the range of low exposures. The halide glasses have the absence of fatigue expected for most photochromic materials; therefore, an unlimited number of recording-erasing cycles have been made with these materials . Finally according to Baldwin,[124] storage capacities of approximatley of $10^9$ bits per millimeter are possible with photochromic materials.

PHOTOCHROMIC LITHIUM NIOBATE ($LiNbO_3$). The photochromic lithium niobate consists of iron and of either manganese or copper-doped crystals that according to Staebler et al.[125] are pulled from melts of the respective materials in a furnace with controlled atmosphere. Although the technical details for preparation of this material are missing in Staebler's report, they are inferred from the description given for preparing iron doped $LiNbO_3$ described below. Unlike the iron doped $LiNbO_3$, the seemingly preferred iron (Fe) and manganese (Mn) doped $LiNbO_3$ (preferred to the iron and copper doped material) are optically reversible. Ultraviolet (UV) light is used initially to produce ionization of the manganese deep electronic trap, resulting in the transfer of an electron to the trivalent iron site and the resulting capture and formation of the now visible light-sensitive divalent iron. Although the mechanisms for these processes are not well defined as of Staebler's writing, irradiation of the divalent iron with visible light restores the crystal to its initial state, and since these are deep traps that are involved, there are no thermal effects at room temperatures. Phase holograms rather than absorption holograms generally expected of photochromic material are generated in $LiNbO_3$, Mn and Fe doped crystals as the result of the electro-optical effect. About 3 to 7 joules per square centimeter required to restore the UV irradiated sample to its initial state. The details for the preparation and the mechanisms in $LiNbO_3$ crystals used as holographic storage medium for both read only and read-write applications are presented next.

Crystals of iron doped $LiNbO_3$ are grown by pulling melts of $Fe_2O_3$ in $LiNbO_3$ in platinum crucibles heated in a resistance furnace. The C-axis growth permitted crystals up to 25 millimeters in diameter to be produced. The crystals are annealed for several hours at reduced temperatures (with the current off) in an oxygen atmosphere. This adjusts the electrolytic reduction of the crystal that occurs during poling. The crystals are nearly colorless after the crystal growth and the cooling down processes are completed. Gamma ($\gamma$) radiation or heating in a reducing atmosphere darkens the crystals. The $LiNbO_3$ crystal doped with 0.0005 percent Fe shows a significant increase in visible light absorption compared to the undoped crystals, both having been irradiated with $\gamma$-radiation. The trivalent iron is believed to be reduced to the divalent from by the $\gamma$-radiation. Reduction of the crystals in argon gas atmospheres can successfully reduce the iron without seriously introducing severe latice reductions.

---

[124] William Y. Baldwin, "Determination of the Information Storage Capacity of Photochromic Glass With Holography," *Applied Optics,* Vol. 6, No. 8, 1967, p. 1428.

[125] David Staebler, William Phillips, and B.W. Faughnan, *Materials For Phase Holographic Storage (U),* RCA Laboratories, Princeton, N.J., PRRL-73-CR-17, March 1973, NTIS: AD-760 343.

The trivalent iron is thought to be the deep electronic trap that captures an electron, forming divalent iron when either $\gamma$-radiation or different reducing heat treatments are applied to iron doped $LiNbO_3$. Irradiation with light at 1.45 electron volts (0.854 micrometers) or greater energy injects a single electron for each photon absorbed by the divalent iron trap into the conduction band and produces the observed photoconductivity. Thus, with visible light irradiation corresponding to the 1.45 electrovolts energy or greater, these electrons migrate to regions of non-irradiated trivalent iron where they recombine with the excess trivalent iron (i.e. iron that has not been reduced by $\gamma$ -radiation or heat treatments) to form again divalent iron. Hence, should this recombination occur in an image-wise fashion, then electric-field effects from the resulting redistribution of the electrons among the deep traps in the crystal must produce a birefringence, or an electro-optical, effect in an image-wise fashion in the crystal. The image can then be observed with suitable polarized light that is sensitive to differences in refractive indices produced in the crystal by the electro-optic effect. Note that the trivalent iron is considered to be empty deep electronic traps that do not absorb light in the visible region near 1.45 electron volts. The divalent iron constitutes the occupied traps that introduce a strong absorption band in the visible region of the spectrum.

The -irradiation or the reducing heating effects produce whole electron pairs in which oxygen is generally thought to give up a pair of electrons to the trivalent iron. Thus, we have

$4Fe^{+3} + 2O^{-2}_{(lattice)} \rightleftarrows 4Fe^{+2} + O_{2(ambient)}$ for an overall reaction.

## SILVER HALIDE, PHASE (BLEACHED)

BACKGROUND. We have seen in the Hardened Dichromated Gelatin section that it is possible to produce very high diffraction efficiency holograms in gelatin without the presence of silver halide. These are volume phase holograms in which the photolysis product, chromic oxide, crosslinks the gelatin protein chains through coordination with carboxyl groups on the chains. Following exposure, the dichromated gelatin layers are dehydrated in a series of alcohol baths. The strain produced in the layer through rapid dehydration of the gelatin promotes formation of cracks in the lesser hardened, unexposed portions of the layer. It is the air, gelatin interfaces that are very efficient in redirecting light into the first order, although the isopropyl alcohol chromium III complex compound formed at the crosslinked sites also contributes to the phase change. In bleached silver halide holograms, generally there are silver halides crystallites distributed in a grating-like structure in the gelatin. The refractive index differences between the respective silver halides and the gelatin promote diffraction of light into the first order. For example, silver chloride, silver bromide, and silver iodide have the refractive indices of 2.071, 2.252 and 2.218 respectively, and gelatin has a refractive index of 1.54. Whereas the hardened dichromated gelatin produces holograms with the more desirable holographic parameters, such as diffraction efficiency and signal-to-noise ratio, it is the bleached silver halide hologram prepared from commercially available plates that has greater photosensitivity, that exhibits good shelf life, and that is easily prepared. Still, it may be possible to produce holograms as variations in the refractive indices exhibit in gelatin alone or as variations in refractive indices of gelatin and air interfaces, as in the hardened dichromated gelatin material, but using the greater sensitivity of the silver halide emulsion. This possibility will be explored later.

COMMERCIAL PHOTOGRAPHIC PLATES. Colburn et al.[126] describe the commercially available photographic plates suitable for holography. Eastman Kodak and Agfa Gevaert are the primary suppliers of these plates. The panchromatic plates include the Kodak 649F, which is a spectroscopic plate, the Kodak 120, which has a special holographic emulsion, and the Agfa Scientia series 8E75, which is similar to the Kodak 649F and the Agfa Scientia Series 10E75 that has a lower resolving power (approximately 2500 lines per millimeter) but 20 to 30 times increased exposure sensitivity. Although it may be special ordered as backed plates, the Kodak 649F plate is usually available as 17-micrometer-thick emulsions or unbacked plates. However, it may be special ordered also as 35-micrometer-thick emulsions on backed or unbacked plates. In contrast to the Kodak plates, all Agfa plates have 6-micrometer-thick emulsions.

The orthochromatic plates include the Kodak 649GH plate and a Kodak High Resolution plate that contains 6-micrometer-thick layers, the Agfa Scientia series 8E56 that is similar to the Kodak 649GH, and the Agfa Scientia series 10E56, which has a lower resolving power (approximately 2,500 lines per millimeter) but 20 to 30 times increased exposure sensitivity. The panchromatic type plates may be exposed with the helium neon laser ( = 632.8 nanometers) and, hence, may be the plates used in preparing bleached silver halide holograms.

ZECH'S BLEACHING METHOD. The sequence and chemistry involved in the processing steps are significant to the type and characteristics of the finished holograms. Thus, these will be examined in detail next. Zech[127] gives a detailed procedure for preparing bleached silver halide holograms. Here the fine grained Lippman emulsions, such as found on many of the above described plates (e.g. Kodak 649F), are exposed, developed, fixed, hardened, refixed, bleached, stabilized, and dried. The developer contains two developing agents, namely p-methylaminophenol sulfate (also known as Elon) and hydroquinone. Ordinarily, the reaction products of these two developing agents are known to tan gelatin or to harden it to varying degrees.

---

[126] W.S. Colburn, R.G. Zech, and L.M. Ralston, *Holographic Optical Elements,* Technical Report AFAL-TR-72-409, Wright-Patterson Air Force Base, Ohio, January 1973.

[127] R.G. Zech, *Data Storage in Volume Holograms,* Doctoral Dissertation, University of Michigan, 1974, pp. 198-200.

The D-19 developer contains considerable sodium sulfite, and as Neblette[128] points out, the tanning action decreases as the concentration of sodium sulfite increases. The degree of hardening of gelatin promoted by D-19 developer may not be much, but since the possibility exists, let's examine the process now. The tanning or hardening of the gelatin occurs in the region of the developing silver grains. Mees and James[129] state that developing agents containing two or more functional groups, such as the hydroquinone, produce reaction products that promote hardening of the gelatin through the formation of crosslinks between amine groups on adjacent lysine side chains on the gelatin protein molecule. These developing agents demonstrate the greatest tanning or hardening ability of those known. The developing agents that contain only one functional group, such as p-methylaminophenol sulfate, promote hardening of the gelatin upon being oxidized during development of the silver halide but to a lesser degree than the hydroquinone-type developers. Since the hardening or tanning of the gelatin forms a relief image as well, one can appreciate the importance of managing this process to benefit hologram porperties. To continue with Zech's method, following development of the holographic plate, the unexposed and remaining silver halide is removed during fixing in Kodak Rapid Fixer. This leaves the hologram stored in silver metal in a gelatin matrix, perhaps hardened to a greater degree in the vicinity of the silver metal. When the silver metal hologram is bleached in a ferric chloride cupric bromide sulfuric acid solution, the silver metal is oxidized to a silver halide that is a mixture of silver chloride and silver bromide. The oxidation of silver metal to silver ion by the ferric ion is thermodynamically favored by virtue of the concentrations of the reactants and products of the reaction. The stabilizer is prepared by mixing solutions of potassium permanganate and potassium bromide in dilute sulfuric acid. The free bromine liberated completes the oxidation of any metallic silver remaining after the bleaching step and, in addition, brominates any reactive sites in the gelatin matrix. The bleached hologram is stabilized to printout a phenomenon in which actinic light reduces the silver halide to free metallic silver and a halogen. Before stabilizing, the halogen would in turn react with the same reactive sites in the gelatin matrix preventing its recombination with the metallic silver, thus promoting the printout phenomenon. It is interesting to note that the bromine liberated in the stabilizing solution may also be used to bleach metallic silver holograms directly.

BROMINE VAPOR BLEACH. The stabilizing effect of bromine in the printout phenomenon associated with the bleached silver halide hologram can also be modified by bleaching metallic silver holograms with bromine vapor. The method is described by Graube.[130] Again, the product is a high diffraction efficiency, volume,

---

[128] C.B. Neblette, ***Photography, Its Materials and Processes,*** 6th Edition, Princeton, N.J. D. Van Nostrand Co., Inc., 1962, p. 237.

[129] C.E. Kenneth Mees, and T.H. James, ***The Theory of the Photographic Process,*** 3d Edition, New York, Macmillan Co., 1966, pp. 304-6.

[130] Andrejs Graube, "Advances in Bleaching Methods For Photographically Recorded Holograms," ***Applied Optics,*** Vol. 13, December 1974.

phase hologram that is not too different from the ones produced by Zech's method. Graube describes a procedure for Kodak 120 backed plates. The exposed plates are developed in Kodak D-19 developer, fixed in Kodak Rapid Fixer with hardener, treated with Kodak photo-Flo, and air-dried. The dried plate containing an amplitude hologram, with an optical density of about four, is placed in a closed vessel containing liquid bromine. The vessel has a volume of approximately 21 milliliters and contains liquid bromine with a surface area of 10 square centimeters in a pool on the bottom of the vessel. Sufficient bromine vapor will evolve in the chamber to bleach the metallic silver hologram in 15 minutes although exposures up to 2 hours have no deleterious effect on the final hologram product. Exposures in excess of 24 to 48 hours promotes severe softening of the gelatin layer. Although comparative studies were made of holograms bleached in chlorine gas, the bromine vapor bleached holograms had twice the diffraction efficiency (i.e. 35 versus 75 percent). This is attributed to the higher index of refraction of the silver bromide. Again, the bromine, vapor-treated, volume phase hologram was demonstrated ability to withstand printout. The reactive sites in the gelatin are oxidized by the bromine vapor blocking their role in the printout process.

IODIDE BLEACHES. We saw that it is possible to produce bleached silver chloride and silver bromide holograms by a direct combination of elemental chlorine or bromine with the metallic silver of an amplitude-type hologram. This is not possible with silver iodide holograms because a direct combination of elemental iodine with metallic silver is not thermodynamically favored. Hariharan and Ramanathan[131] disclose that it is possible to produce holograms with silver iodide dispersed in a gelatin matrix by several methods. One technique consisted of using potassium iodide with an oxidant to bleach metallic silver holograms. Another consisted of converting silver chloride or silver bromide to the corresponding silver iodide by soaking the reversed bleached hologram in potassium iodide. In the first technique, a modified Kodak R-10 bleach is used in which the oxidant is ammonium dichromate with sulfuric acid. A small quantity of potassium iodide (1 gram per liter of bleach solution is added).Too large a quantity of the iodide dissolves the silver compound through formation of a water soluble complex compound of silver iodide. The second technique consists of reversal bleaching of the exposed and developed, but unfixed, metallic silver, silver-halide hologram. Here Kodak type R-9 bleach containing only potassium dichromate and sulfuric acid in solution is used to dissolve the metallic silver, leaving the silver halide (e.g. bromide or chloride) intact. The bleached plate is then soaked in about 0.2 percent-solution of potassium iodide or tetramethylammonium iodide, which forms silver iodide from the silver bromide or chloride. The latter technique is reported to give holograms with better definition than those obtained by the former method. Also, silver iodide exhibits greater resistance to the formation of printout silver than either silver chloride or silver bromide.

---

[131] P. Hariharan and C.S. Ramanathan, "Suppression of Printout Effect in Photographic Phase Holograms," *Applied Optics*, Vol. 10, No. 9 September 1971, pp. 2197-2199.

REVERSAL BLEACHING METHOD. Lamberts and Kurtz[132] describe a reversal bleaching process in which tanning of the gelatin is promoted in the region were the metallic silver is developed out. The tanning is promoted by both the developer used and the particular bleach used. The reversal bleaching process consists of developing in Kodak special developer, SD-48, bleaching without fixing in Kodak R-9 bleach, clearing in solution A Kodak S-13 stain remover followed by Solution B Kodak S-13 stain remover, and drying. The Kodak special developer contains pyrocatechol, which is a developing agent known to promote tanning of the gelatin in the vicinity of the developed metallic silver. The sodium sulfite contained in the developer is a small quantity that preserves the developer from atmospheric oxidation, while not counteracting the tanning action of the pyrocatechol. The sodium sulfate in the developer prevents excessive swelling of the gelatin during development. The spatially varying optical path of the plate with recorded spatial frequencies below 200 lines per millimeter were measured and were found to approach zero at the higher exposures. Apparently, the tanning developer is effective in reducing a collapse of the gelatin in the developed sites. This may be augmented by the Kodak R-9 bleach with its postassium dichromate and sulfuric acid solution that also promotes crosslinking of the gelatin in the development sites. Unlike Kodak R-10 bleach that converts metallic silver to its corresponding silver halide, Kodak R-9 bleach simply dissolves the metallic silver leaving the unfixed silver halide intact. The clearing solution A oxidizes the brown stain gelatin entity formed by the pyrocatechol developing agent reducing the discoloration. Solution B, containing sodium bisulfite, reduces any of the highly colored potassium permanganate remaining in the emulsion. The reversal bleaching processs reduces the amount of scattering or flare attributed to the surface irregularities in the gelatin that are reduced in other holograms when the emulsion surface is immersed in a liquid with a gelatin matching refractive index of 1.54.

REVERSED BLEACHED AND FIXED ALL GELATIN HOLOGRAM. With the apparent extent of hardening and/or tanning occuring in the development sites of emusions processed by the reversal bleach method, it may be possible to prepare a hologram completely free of any silver halide and in which the hologram is formed as variations in the index of refraction in the gelatin emulsion. Further, a hologram formation approximating that of the hardened dichromated gelatin may be realized upon proper dehydration of a reversal bleached and fixed hologram. To explain, using the reversal bleaching process consisting of developing, bleaching without fixing, and clearing followed then by fixing, dehydrating, and drying would produce a photographic plate that is free of all silver and silver halide, and whose gelatin may exhibit the modulation if refractive indices in gelatin that correspond with a hologram fringe pattern. Developing in Kodak special developer SD-48 would promote tanning in the regions of silver metal formation and would be accompanied with stain associated with a pyrocatechol tanning developing agent. It is possible that Kodak developer D-19, or

---

[132] **R.L. Lamberts and C.N. Kurtz, "Reversal Bleaching For Low Flare Light in Holograms,"** ***Applied Optics,*** **Vol. 10, No. 6, June 1971, pp. 1342-1347.**

D-19 with reduced quantities of sodium sulfite, can be used with reliance being made on the reversal bleach, potassium dichromate in sulfuric acid solution, to tan the gelatin in the sites where metallic silver exist. Should this occur, fixing in Kodak Rapid Fixer following any treatment with stain remover would produce the completely cleared gelatin emulsion with a hologram recorded as variations in refractive indices. Dehydrating the holographic plate in appropriate alcohol solutions may even produce the same cracks in the regions of lesser hardened gelatin as observed in the hardened dichromated gelatin hologram. The goal of such a holographic plate then would be to produce not only a hologram whose holographic properties approximate those of hardened dichromated gelatin, but also one that exhibits the storage life, photographic speed, and spectral response of the original silver halide photographic emulsion. Further, the hardened silver halide gelatin hologram would not exhibit the printout phenomenon of the bleached silver halide hologram. Also, it may be possible to reduce the degree of scatter and shrinkage of the layer through proper formulation and control of the processing chemicals.

## REVIEW

This report on holographic recording materials systematically evaluates photosensitive recording materials for use in holographic and other coherent optical systems. The detailed literature search has produced information about process mechanisms, chemistry, methods of preparation, and the nature of the image recording that will be useful in guiding future development of photosensitive recording materials for holographic information in coherent optical systems.

Although the report describes non-silver recording materials in some detail, the silver recording materials are treated more generally. In addition applications of the different holographic recording materials to specific recording problems are described where possible. Also, evalutations are made of different recording materials as to suitability for off-axis holography with indications as to how the materials may be imporved. In summary, over one hundred references are given.

The list of holographic recording materials in this report is not exhaustive. However, the recording materials selected for this review offer either the most promise for storage of topographic information in the near future or a particular advantage in hologram properties, in the storageability of materials, or in uniqueness of application. Additional supplemental reviews are expected to be prepared of the materials not treated in this report. Using silver halide Lippmannn emuslions in off-axis holography is prompted by the greater spectral sensitivity, photosensitivity, and familiarity of processing, while still possessing the capability of recording the high spatial frequencies used in holography. It is the silver halide crystallite and the development of this exposed entity that produces the great amplification of the light effect and makes the silver halide layers unique among all photosensitive materials. There may be $10^6$ metal silver atoms or more produced in the developed crystallite for each photon that is absorbed. Although many photosensitive materials produce only one photolytic molecule for each photo absorbed, others produce hundreds or thousands of photolytic molecules for each photo absorbed. There may be one class of photographic materials that has the photosensitivity of the silver halide emulsions, but even these materials may be limited in the spatial frequencies that they can record. Whereas it is the spectral sensitivity and photosensitivity that makes silver halide useful in off-axis holography, there are other characteristics of certain non-silver halide photographic materials that enable them to be used in ways that silver halide layers are incapable of. These materials and their properties will be described next.

ELECTROSTATIC IMAGING PROCESSES. The electrostatic imaging processes are the photographic processes whose photosensitivity more nearly equals that of the silver halide Lippmann emulsions. Developing electrostatic latent images on exposed photoconductive surfaces using liquid immersion development may produce resolutions in excess of 1,000 lines per millimeter. The processing steps of corona charging, exposing, developing, and fixing may be carried out rapidly, producing imagery within a minute or less. The potential hologram may be either the absorption or phase type, depending upon the composition of the liquid developers and upon the type of photoconductor (e.g. whether a transparent photoconductor is used or not). The imagery produced may exist as a singular layer of submicrometer particles on the photoconductive surface, and thus unlike silver halide emulsions with photosensitive layers many micrometers thick, it may exist in a more nearly planar configuration.

Another electrostatic imaging process uses a photosensitive photoplastic film usually made of transparent organic photoconductor deposited on a transparent conducting layer on a film base. Over the photoconductive layer is deposited still another thin layer of an insulating thermoplastic. An electrostatic latent image produced by a plane wave, interference pattern deforms the thermoplastic layer during heating, producing a corresponding pattern as surface variations in the thermoplastic layer. Spatial frequencies approximatley 1,000 millimeters$^{-1}$have been demonstrated in this phase surface, holographic recording medium. In addition to its completely dry processing, the photoplastic film also possesses a write, erase capability. Heating the photoplastic film with recorded images to higher temperatures than used in recording restores the recording media to its initial state. A new image may be recorded, and the cyclic process may be repeated many times.

PHOTORESISTS. The photoresists are photosensitive materials that produce phase surface holograms. Here exposure to actinic radiation produces chemical changes in the photoresist layer that enables differentiation with certain solvents. In negative working layers, the exposed material becomes insoluble in the solvent that dissolves the unexposed regions, and in positive working layers, the exposed material is soluble in the solvent that the unexposed regions are insoluble in. High spatial frequency gratings may be prepared in photoresist, particularly thin layers of positive photoresist, that in turn may be used to accomplish many different things. The vapor deposition of nickel on the holographic grating in photoresist produces a nickel master from which replication of the grating may be made rapidly in thermoplastic using a heated embossing technique. The Radio Corp. of America (RCA) has replicated multicolor maps prepared as three-color separations in positive photoresist in this manner for their holographic moving map display. Once the nickel master is prepared, there is no simpler method for producing full color transparencies for projection than by this embossing method. The positive photoresist is used to make holographic diffraction gratings. The gratings thus prepared by using the interference pattern formed in two overlapping beams of coherent light are free of ghost images and high stray light levels characteristic of ruled diffraction gratings. The holographic grating has important applications in vacuum ultraviolet spectroscopy. Production of iron oxide holograms using techniques in positive photoresists holographic recording produces an archival storage media that is dimensionally stable in ambient atmospheres. Substitution of a reflective metal, such as aluminum, for the iron oxide would produce holograms with the same dimensional stability, but with the capability of either reflecting or transmitting the light incident upon it. The heat build up in this type of recording material when exposed to high intensity light sources would be much less than in corresponding absorption type holograms or silver images on film or glass plates.

HARDENED DICHROMATED GELATIN. The hardened dichromated gelatin plate produces a hologram well known for its high diffraction efficiency and signal-to-noise ratio. Because of its poor shelf life, the dichromated gelatin plate and, for that matter, any dichromated protein emulsion (e.g. egg albumen, zein, or casein) or polymer emulsions cannot be commercialized. These materials must be prepared shortly before use. The patent literature demonstrates that the use of diazos, diazo-oxides, and azides enables preparation of stable photosensitive materials with sufficient shelf life to permit commercialization, and these materials have widely replaced the use of dichromated photosensitive materials in the printing industry. The same may happen to using dichromated materials in holography. Perhaps, the first of the improved shelf life materials used in holography is the Shipley AZ 1350 positive photoresist. This important photoresist is believed to contain a diazo-oxide photosensitizer in a mixture of Novolak resins and alkali-resistant resins. The Shipley photoresist has been used in the production of holographic diffraction gratings and in the RCA method for making full color holograms using the embossing technique. Other methods may be found to use the diazos, diazo-oxides, and azides to produce holograms with many of the properties of the hardened dichromated gelatin, but with improved shelf life typical of materials prepared with one of these three types of photosensitive compounds.

There may be an alternate method for producing an all-gelatin hologram with many of the properties of the hardened dichromated gelatin. This method would take advantage of the photosensitivity and spectral response of the silver halide emulsion, but rather than producing crosslinking in the gelatin by photolyzing dichromate used in the hardened dichromated gelatin layer, the crosslinking of the gelatin would be promoted by the tanning developers and the dichromated reversal bleaches. The developers and bleaches would promote crosslinking of the gelatin in the same image-wise fashion as the dichromate in hardened gelatin. It may be possible to produce the same cracks in the lesser hardened regions as in hardened dichromated gelatin upon drying the exposed layer in the different alcoholic baths. The new type of gelatin hologram would demonstrate archival properties as far as the recorded image properties are concerned, but as with most gelatin holograms it may lack good geometric fidelity in any reconstructed images.

PHOTOPOLYMERS. The photopolymer materials have photosensitivities that are greater than the photoresists and photochromic materials, but that are not as great as the silver halide emulsions. This is promoted by the chain reaction that occurs in the photosensitive monomer solution that produces polymers consisting of a number of thousands of monomer units. The holograms produced are of the phase type with either modulations in refractive indices in the bulk of the layer or as modulations in the surface. The photopolymers have the additional advantage of a completely dry and rapid processing. There is reason to believe that fully developed photopolymers would have good shelf life and produce images with archival properties and good geometric fidelity.

PHOTOCHROMIC MATERIALS. The photochromic materials are capable of extremely high spatial frequency recordings that can be easily erased with radiation of a different wave length than used to record with. The materials have extremely low photosensitivity, but may exhibit a very good dynamic range. Processing is completely dry since light is the only energy needed to record and to erase an image on a layer of the material. Also, there are photochromic materials that can be fixed (so called fixable photochromics) in acidic atmospheres.

SILVER HALIDE, PHASED (BLEACHED). One of the major problems with bleached, silver halide holograms is the print-out phenomena exhibited by the silver halide. In this, the photolyzed halogen, produced upon subsequent exposure of the hologram, reacts with the gelatin leaving an accumulation of metallic silver that increases with exposure. The silver halide then darkens with the increasing concentrations of silver metal in the emulsion. Different methods are being used to minimize the print-out phenomena. The most promising method uses bromine vapor to bleach the silver metal image. The bromine vapor also brominates any reactive sites in the gelatin and produces a bleached image with greatly reduced print-out property. Apparently, any photolyzed bromine is trapped and allowed to reunite with the metallic silver upon cessation of illumination, or else bromine is not produced from the silver bromine in gelatin thusly brominated. Still, another problem arises from the scattering produced by the bleached silver halide image that is found to increase with exposure. This problem is solved in the completely gelatin hologram as in the hardened dichromated gelatin.

## CONCLUSIONS

1. In the bleached, silver halide hologram excellent recording capability is obtained (i.e. photographic sensitivity and spectral sensitivity), but a lack of archival storage results because of the print-out phenomena.

2. The hardened dichromated gelatin hologram exhibits the highest diffraction efficiency and signal-to-noise ratio of any holographic recording material known. In addition, this material lacks storage ability needed for commercialization. Also, it is difficult to obtain constant results in preparing the hologram.

3. The photoresists produce phase surface holograms that are unique in their applications. For example, the Shipley positive photoresist AZ 1350 has proven useful in the production of multicolor maps in thermoplastic in the RCA holographic moving map display and in the production of holographic diffraction gratings. However, the photoresists lack the photographic and spectral sensitivity needed for easy preparation, such as enjoyed by the silver halide holograms. Because they do produce holograms with good archival storage and quality, the photoresists have a greater potential in holographic storage.

4. The photopolymers have a greater photographic and spectral sensitivity than the photoresists. They also demonstrate a good materials storage ability, image archival quality, and completely dry processing techniques. The photopolymers are among the best materials for holographic storage.

5. Among the electrostatic imaging processes, the photoconductive thermoplastic, or photoplastic, material demonstrates the photographic and spectral sensitivity of the silver halide Lippmann emulsions. Also, the material uses dry processing techniques, may be erased wtih heat, and may be recycled many times. Even though the processing parameters are difficult to control, the material has a greater potential for holographic storage.

6. The photochromic materials are capable of extremely high spatial frequency recordings, and they may be recycled indefinitely using a dry processing technique (i.e. active light). Although the materials are the least photosensitive, they can be used to write and erase holographic imagery, that is to recycle indefinitely.

# BIBLIOGRAPHY

Akagi, Motoo, "Spectral Sensitization of Dichromated Gelatin," *Photographic Science and Engineering,* May/June 1974.

Albrecht, J., Epping, R.H., *Investigations on the Transfer of Full-Tone Reproduction in Electrophotography,* Translation No. T-1929-68, U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va., 22060, 1968, NTIS AD-837-289.

Baldwin, William Y., "Determination of the Information Storage Capacity of Photochromic Glass With Holography," *Applied Optics,* Vol. 6, No. 8, 1967.

Bartolini, R.A., "Characteristics of Relief Phase Holograms Recorded in Photoresists," *Applied Optics,* Vol. 13, January 1974.

Boersma, Theo Tjalka, "Method of Manufacturing Metallic Patterns," U.S. Patent 2,819,164, 7 January 1958.

Booth, B.L., "Photopolymer Material For Holography," *Applied Optics,* Vol. 14, No. 3, March 1975.

Borchers, Henning H., Steppan, Helmut, Uhlig, Fritz, "Process For the Preparation of A Printing Plate Presensitized With A Diazonium Salt," U.S. Patent 3,510,307, 5 May 1970.

Caton, Thomas R., "Light-Sensitive Coating and the Method For Its Production, " U.S. Patent 2,921,852, 19 January 1960.

Cerwonka, Edward, J., "Dye-Sensitized Photo-Polymerization Process, U.S. Patent 3,615,452, 26 October 1971.

Chang, Milton, "Dichromated Gelatin of Improved Optical Quality," *Applied Optics,* Vol. 10, November 1971.

Christensen, Carl W., "Light-Sensitive Naphthoquinone Diazide Composition Containing A Polyvinyl Ether," U.S. Patent 3,634,082, 11 January 1972.

Christensen, Carl W., Issacson, C.M., "Light-Sensitive Quinone Diazide Composition With N-3-Oxohydrocarbon Substituted Acrylaminde," U.S. Patent 3,900,325, 19 August 1975.

Ciafone R. F., Ed., "Optical Storage and Display Media," *RCA Review,* Vol. 33, No.1, March 1972.

Clark, Kenneth G., "Photoresist Techniques in Microelectronics," in R.J. Cox (Ed.), *Non-Silver Photographic Processes,* New York, Academic Press, 1975.

Close, D.H., Graube, A., *Holographic Lens For Pilot's Head-Up Display,* Hughes Research Laboratory, Malibu, California, N-6229-73-0388, August 1974, NTIS: AD-787 605.

Colburn, W.S., Haines, K.A., "Volume Hologram Formation in Photopolymer Materials," *Applied Optics,* Vol. 10, No. 7, July 1971.

Colburn, W.S., Zech, R.G., Ralston, L.M., *Holographic Optical Elements,* Technical Report AFAL-TR-72-409, Wright-Patterson Air Force Base, Ohio, January 1973.

Collier, R.J., Burckhardt, C.B., Lin, L.H., "Hologram Recording Materials," *Optical Holography,* New York, Academic Press, Chapter 10 1971.

Cox, R.J. Ed., *Photographic Gelatin,* New York, Academic Press, 1972.

Credelle, T.L. Spong, F.W., "Thermoplastic Media For Holographic Recording," *RCA Review,* Vol. 33, March 1972.

Curran, R.K., Shankoff, T.A., "The Mechanism of Hologram Formation in Dichromated Gelatin," *Applied Optics,* Vol. 9, July 1970.

Dearnaley, A.M. Stoneham, Morgan, D.V., "Electrical Phenomena in Amorphous Oxide Films," *Reports on Progress in Physics,* 1971.

Delzenne, Gerard Albert, "Production of Light-Sensitive Coatings For Use in the Manufacture of Copying Materials Such as Printing Plates," U.S. Patent 3,501,296, 17 March 1970.

Deutch, Albert S., Loprest, Frank J., "Positive-Working Diazo-Oxide Terpolymer Photoresists," U.S. Patent 3,637,384, 25 January 1972.

DiBlas, Umberto, Franco, Simone, "Offset Printing Positive Diazo Presensitized Matrixes Containing Photosensitive Quinone Diazide and A Resin Binder," U.S. Patent 3,551,154, 29 December 1970.

Dowdall, J.F., Case, J.M., "Planographic Printing Plate," U.S. Patent 3,136,636, 9 June 1964.

Eastes, J.W., Gillespie, H.C., Wielicki, H., "Draft Specifications for Multicolor Electrostatic Printing Materials," *TAPPI*, Vol.52, No. 5, May 1969.

Efros, I.S., Urres, T., Lyalikov, K.S., Kovalera, K.A., "The Mechanism of the Light Hardening of Polymers With Azides," Translated From Russian by U.S. Army Foreign Science and Technology Center, AD-727-964, July 1971.

Endermann, Fritz, Neugebauer, Wilhelm, Reichel, Maximilian Karl, "Light-Sensitive O-Quinone Diazides and the Photomechanical Preparation of Printing Plates Therewith," U.S. Patent 3,148,983, 15 September 1964.

Epping, Reinhold H., *About the Dependence of the Photoconduction on the Molecular Weight of Poly-N-Vinylcarbozole,* University of Munich, 1970.

Fauser, D.L., Walecka, J.A., *Development of Image Forming Materials,* U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, NTIS AD-430-090L, 1963.

Frank, C.W., Buchacek, R., *A Study of the Effect of Corona Conditions on Electrostatic Printing Processes,* U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va., 22060, ETL-CR-72-17, AD-755-259, 1972.

Gillespie, H.C., "Magnetic Brush Reversal Powder Development on Zinc Oxide-Binder Layers," *2d Symposium on Unconventional Photographic Systems*, Washington, D.C., 26-28 October, 1967.

Gillespie, H.C., Lee, W.M., Lozier, G., *Continuous-Tone Electrophotography*, U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va. 22060, NTIS AD-673-881, August 1968.

Gladden, James W., Chen, Pi-Fuay, *Investigation of Continuous Photoconductive Layer Arrays*, U.S. Army Engineer Laboratories, Ft. Belvoir, Va. 22060, ETL-0011, AD-A010 642, May 1975.

Goetz, G., Mueller, R.K., Shupe, D.M., "Recent Progress in a Real-Time 3-D Display," *Proceedings of IEEE Conference on Display Devices*, New York, October 1972.

Graube, Andrejs, "Advances in Bleaching Methods For Photographically Recorded Holograms," *Applied Optics*, Vol. 13, December 1974.

Grime, G.W., "Holographic Diffraction Gratings Recorded In Photoresist," in R.J. Cox (Ed.), *Non-Silver Photographic Processes*, New York, Academic Press, 1975.

Hannan, W.J., et al., *J. Soc. Motion Pict. Telev. Eng.*, Vol. 82, 1973.

Hariharan, P., Ramanathan, C.S., "Suppression of Printout Effect in Photographic Phase Holograms," *Applied Optics*, Vol. 10, No. 9 September 1971.

Heiland, G., Mollwo, E., Stockmann, F., "Electronic Processes in Zinc Oxide," *Solid State Physics*, Vol. 8, Academic Press, 1959.

Hepher, M., "The Photo-Resist Story - From Niepce To The Modern Polymer Chemist," *J. of Photographic Science*, Vol. 12, 1964.

Hodgins, George R., "Developer Composition For A Light-Sensitive Lithographic Plate," U.S. Patent 3,091,533, 28 May 1963.

Holstead, Colin, Langley, Abbotts, Prezezdziecki, Wojciech Maria, "Azide Sensitizers and Photographic Elements," U.S. Patent 3,617,278, 2 November 1971.

Hwang, HoChien, "Diazo Compound For Lithographic Plates," U.S. Patent 3,544,323, 1 December 1970.

Jenney, J.A., "Holographic Recording With Photopolymers," *J. Opt. Soc. Am.* Vol. 60, 1970.

Jewett, C.L., Case, J.M., "Planographic Printing Plate," U.S. Patent 2,714,066, 26 July 1955.

Kalle AG, "Improvements In and Relating to Reprographic Materials," British Patent 1,223,570, 24 February 1971.

Klein, Otto C., *Research in Continuous Tone Electrophotography*, U.S. Army Engineer Topographic Laboratories, Ft. Belvoir, Va., 22060, NTIS AD-101-863, December 1962.

Kobayashi, Kesanao, "Light-Sensitive Lithographic Plate," U.S. Patent 3,635,709, 18 January 1972.

Kokado, H., Ohba, Y., Inoue, E., "Galvonic Cell Type Electrophotography Utilizing Photoconductive Memory of ZnO-Resin Layers," *Fourth Society of Photographic Scientists and Engineers Conference on Unconventional Photographic Systems,* Arlington, Va., 21 November 1975.

Kosar, Jaromir, *Light-Sensitive Systems: Chemistry and Application of Non-Silver Halide Photographic Processes,* New York, John Wiley and Sons, 1965.

Kurtz, Robert L., Owen, Robert B., "Holographic Recording Materials - A Review," *Optical Engineering,* Vol 14, No. 5, September-October 1955.

Laridon, Urbain Leopold, "Copying Material For Use In the Photochemical Preparation of Printing Plates," U.S. Patent 3,495,979, 17 February 1970.

Laridon, Urbain Leopold, "Copying Material For Use In the Photochemical Preparation of Printing Plates," U.S. Patent 3,494,767, 10 February 1970.

Lawson, Leslie Edward, Smith, Frank E., Smith, Peter John, "Solvent Development of Light Sensitive Diazo Layers," U.S. Patent 3,634,086, 11 January 1972.

Levinos, Steven, "Offset Printing Plates," U.S. Patent 3,474,719, 28 October 1969.

MacDonald, R.I., Hill, K.O., "Evaluation of A New Photopolymer Hologram Recording Medium," Communications Research Center, Ottawa, Canada, NTIS Report No. N-73-32395, September 1973.

Mainthia, Shashi B., "Diazo-Polyurethane Light-Sensitive Composition," U.S. Patent 3,660,097, 2 May 1972.

Margerum, J.D., Tenorio, A.M., Petrusis, C.T., Little, M.J., "Studies on the Mechanism of Dye-Sensitized Photopolymerization Initiation," *Polymer Preprints For the 160th American Chemical Society Meeting,* Chicago, Ill., 15 September, 1970.

Mees, C.E. Kenneth, James, T.H., *The Theory of the Photographic Process,* 3d Edition, New York, Macmillian Co., 1966.

Merrill, Stewart H., Unruh, Cornelius C., "Azidophthalic Anhydrides," U.S. Patent 3,002,003, 26 September 1961.

Meyerhofer, Dietrich, "Phase Holograms in Dichromated Gelatin," *RCA Review,* Vol. 33, March 1972.

National Academy of Sciences, Report of the AdHoc Committee on the *Fundamentals of Amorphous Semi-Conductors,* (National Materials Advisory Board, National Research Council), 1972.

Neblette, C.B., *Photography, Its Materials and Processes,* 6th Edition, Princeton, N.J., D.Van Norstrand Co., Inc., 1952.

Neugebauer, William, Stephan, H., Rebenstock, A., "Presensitized Foil For Planographic and Offset Printing," U.S. Patent 3,235,382, 15 February 1966.

Neugebauer, Wilhelm, Endermann, Fritz, "Naphthoquinone Diazide Lithographic Material and Process of Making Printing Plates Therewith," U.S. Patent 3,106,465, 8 October 1963.

Neugebauer, Wilhelm, Endermann, Fritz, Reichel, Maximilian Karl, "Etchable Reproduction Coatings On Metal Supports," U.S. Patent 3,201,239, 11 January 1972.

Norman, S.L., Singh, M.P., "Spectral Sensitivity and Linearity of Shipley AZ-1350J Photoresist," *Applied Optics,* Vol. 14, April 1975.

Nuttall, R.H., "The Infra-Red Spectra of Some Stable Diazonium Salts," *Spectochimica Acta,* Vol.17, 1964.

Okamoto, K., Kusabayashi, S., Yokayama, M. Mikawa, H., "Current Research on Organic Photoconductors for Electrophotography," *2d International Conference on Electrophotography,* Washington, D.C., 24-27 October, 1973.

Oliphant, W.D., "Xerography: A Non-Chemical Photographic Process," *Discovery* Vol. 14, 1953.

Peterson, Willard D., Fabian, Robert W., "Photographic Reliefs Made By Means of Transfer Intermediaries Which Produce Gas Upon Irradiation," U.S. Patent 3,093,478, 11 June 1963.

Philips Lamps Ltd., London, "Improved Method of Producing Photographic Contrasts By Means of A Diazonium Compound," British Patent 534,341, 5 March 1941.

Poot, Albert Lucien, "Radiation-Sensitive Recording Material," U.S. Patent 3,493,371, 3 February 1970.

Pouradier, J., Burness, D.M., "The Hardening of Gelatins and Emulsions," in T.H. James (Ed.) *The Theory of The Photographic Process,* New York, Macmillian Co., 1966.

Powers, Austin J., Jr., "Development of Diazo and Azide Sensitized Colloids," U.S. Patent 2,690,968, 5 October 1954.

Pries, Lawrence L., "Light Sensitive Plate Coating," U.S. Patent 2,858,214, 28 October 1958.

Rauner, Frederick J., Arcesi, J.A., Guild, J.R., "Light Sensitive Quinone Diazide Polymers and Polymer Composition, " U.S. Patent 3,647,443, 7 March 1972.

Reynolds, George A., "Photosensitive Compounds and Elements," U.S. Patent 3,519,424, 7 July 1970.

Rouse, Edward, "Improvements In or Relating To Photogravure Processes," British Patent 859, 781, Patent Provisional Specification No. 33841, 25 January 1961.

Ruckert, Hans "Reprographic Copying Composition," U.S. Patent 3,455,914, 15 July 1969. "Reprographic Copying Composition," U.S. Patent 3,539,559, 10 November 1970. "Azido Azomethines For Reprographic Copying Compositions," U.S. Patent 3,558,609, 26 January 1971.

Schelly, Zoltan A., "Effect of the Solvent on the Kinetics of Diazotization," Air Force Office of Scientific Research, Arlington, Va., AD-721-766, January 1970.

Schmidt, Maximilian P., Sus, Oskar, "Quinone Diazides For Use In Reproduction Materials," U.S. Patent 2,994,608, 1 August 1961.

Schmidt, Maximilian P., "Process of Making Printing Plates and Light Sensitive Material Suitable For Use Therein," U.S. Patent 3,046,118, Formulae 20 and 21, 24 July 1962.

Silver, Julius L., "Printing Plate Composition," U.S. Patent 3,615,532, 26 October 1971.

Slack, C.T., "Calculations of the Response Curve of a Solid Photochromic Film," *Optica Acta*, Vol. 17, No. 7, July 1970.

Smith, M.P., Zahn, R., "Diazo Compounds and A Process of Preparing Them," U.S. Patent 2,063,631 8 December 1936.

Staebler, David, Phillips,William, Faughnan, B.W., *Materials For Phase Holographic Storage (U)*, RCA Laboratories, Princeton, N.J., PRRL-73-CR-17, NTIS AD-760-343, March 1973.

Stein, Kenneth J., "Holographic Map Display Developed," *Aviation Week and Space Technology*, 22 April 1974.

Steinhoff, Thomas L., Shipley, Charles R., Jr., MacDonald, John A., "Light Sensitive Naphthoquinone Diazide Composition and Material Containing an Alkali Insoluble Polymer," U.S. Patent 3,402,044, 17 September 1968.

Streifer, W.M., Stark, Howard, "Some Theoretical Aspects of High Resolution Xerographic Development," *Applied Optics*, Supplement 3: Electrophotography, 1969.

Sus, Oskar, "About The Nature of The Photolysis Product of The Diazo Compounds. Contraction of An Aromatic 6-Member Ring To A 5-Member Ring," *Liebigs Annalen der Chemie*, Vol. 556, 1944.

Sus, Oskar, Uhlig, Fritz, "Naphthoquinone Diazide Sulfonic Acid Ester," U.S. Patent 3,640,992, 8 February 1972.

Takeishi, Makoto, Okawara, Makoto, "Synthesis and Reaction of Polyvinyl Chloride Containing Azide Group," *J. of Polymer Science, Part B*, Vol. 7 No. 3, March 1969.

Thomsen, Milton S., Bube, Richard H., "High-Sensitivity Photoconductor Layers," *Review of Scientific Instruments*, Vol. 26, No. 7, July 1955.

Thompson, B.J., "Resolution in Images Formed Holographically - A Summary," Unpublished Tutorial Paper, May 1977.

Tomlinson, W.J., Clandross, E.A., Weber, H.P., Aumille, G.D., "Multicomponent Photopolymer Systems For Volume Phase Holograms and Grating Devices," *Applied Optics,* Vol. 15, No. 2, February 1976.

Tsekhomskii, V.A., Tunimanova, I.V., "Photochromic Glasses," Translation From *Transactions of the 1st All-Union Conference on Non-Silver and Novel Photographic Processes,* Section IV, Kiev, Ukrainian SSR, 1972.

Urbach, John C., "Advances in Hologram Recording Materials," *Proceedings of the Society of Photo Optical Instrumentation Engineers,* Vol. 25, April 1971.

Wai-Hon, Lee, "Effect of Film-Grain Noise on the Performance of Holographic Memory," *J. of Opt. Soc, of Amer.,* Vol 62, No. 6, June 1972.

Walkup, Lewis E., "Method For Developing Electrostatic Images," U.S. Patent 2,784,109,

Walkup, Lewis E., Wise, Edward N., "Developer Composition For Developing an Electrostatic Latent Image," U.S. Patent 2,638,416, assigned to Battele Development Corp.

Wilcox, David H., "History of the Use of Sodium Nitrite in the Diazotization Reaction," *American Dyestuff Reporter,* 24 October 24 1966.

Whitear, Brian R.D., Fry, Douglas James, "Litho Plate," U.S. Patent 3,589,898, 29 June 1971.

Zandstra, P.J., Evleth, E.M., "Photolytic Decomposition of Aryldiazonium Salts. The p-Dimethylaminophenoxy Radical," *J. Amer. Chem. Society,* Vol. 86, 1964.

Zech, R.G., *Data Storage in Volume Holograms,* Doctoral Dissertation, University of Michigan, 1974.

Zech, R.G. *Holographic Recording Materials,* Technical Report, F 30602-74-C-0030, Rome Air Development Center, Griffiss AFB, New York, July 1974.

Zech, R.G., Dwyer, J.C., Fichter, H., Lewis, M., "Heat Processed Photoresist For Holographic Data Storage Applications," *Applied Optics,* Vol. 12, December 1973. Also Final Technical Report No. F 30602-74-C-0030, Rome Air Development Center, Griffiss AFB, New York, July 1974.

Zemp, Rene Robert, "Process For Producing Images," U.S. Patent 2,729,562, 3 January 1956.

Zollinger, Heinrich, Nursten, Harry E., Ed. and Trans., *Azo and Diazo Chemistry Aliphatic and Aromatic Compounds,* Interscience Publishers, New York, 1961.