

UNCLASSIFIED

AD 296 087

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY ASTIA
AS AD #296087

Investigation of Photopolymerization Process

Fourth Quarterly Report

15 AUGUST 1962 - 14 NOVEMBER 1962

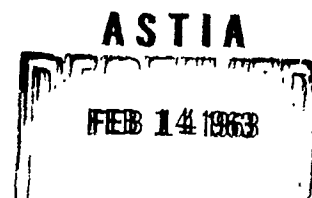
296 087

Signal Corps Contract DA 36-039-sc-88933

File Number 00528-PM-62-91-91 (2350)

PR & C Number 62-ELS/R-2350 (61/2355)

Placed by
U. S. ARMY ELECTRONICS MATERIEL AGENCY
Fort Monmouth, New Jersey



Contractor
ANSCO DIVISION
GENERAL ANILINE & FILM CORPORATION
Binghamton, New York

NO OTS

General Aniline & Film Corporation
Ansco Division
Binghamton, New York

Copy No. 13 of 65 copies

"Investigation of the Photopolymerization Process"

Fourth Quarterly Report

15 August 1962 - 14 November 1962

Object: To conduct a research investigation of
photopolymerization techniques and their
utilization as a dry picture-taking and
printing medium for military use.

Signal Corps Contract No.: DA 36-039-sc-88933
File No.: 00528-PM-62-91-91 (2350)
PR&C No.: 62-ELS/R-2350 (61/2355)

Project Manager: Steven Levinos

Staff: E. Cerwonka
F. W. Millard
S. Levinos

Report Prepared by: E. Cerwonka
F. W. Millard

AD _____	Accession No. _____	Unclassified
ANSCO, Division of General Aniline & Film Corporation, Binghamton, N.Y.	Investigation of the Photopolymerization Process-	1. Investigation of Photopolymerization Process.
E. Cerwonka and F.W. Millard	Fourth Quarterly Progress Report, 15 August 1962 to 14 November 1962	2. Signal Corps
Signal Corps Contract DA 36-039-sc-88933 File No. 00528-PM-62-91-91 (2350) - Unclassified Report		Contract DA 36-039-sc-88933
Polymerization of light-exposed areas of coated layers comprised of a light-sensitive ferric salt of a phenolic alpha hydroxy acid, a monomer and a cellulose derivative as binder was found to take		

AD _____	Accession No. _____	Unclassified
ANSCO, Division of General Aniline & Film Corporation, Binghamton, N.Y.	Investigation of the Photopolymerization Process-	1. Investigation of Photopolymerization Process.
E. Cerwonka and F.W. Millard	Fourth Quarterly Progress Report, 15 August 1962 to 14 November 1962	2. Signal Corps
Signal Corps Contract DA 36-039-sc-88933 File No. 00528-PM-62-91-91 (2350) - Unclassified Report		Contract DA 36-039-sc-88933
Polymerization of light-exposed areas of coated layers comprised of a light-sensitive ferric salt of a phenolic alpha hydroxy acid, a monomer and a cellulose derivative as binder was found to take		

TABLE OF CONTENTS

	<u>Page</u>
A. PURPOSE	1
B. ABSTRACT	2
C. PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES	3
D. FACTUAL DATA	4
E. PROGRAM FOR NEXT INTERVAL	23
F. IDENTIFICATION OF KEY TECHNICAL PERSONNEL	24

A. PURPOSE

The general objective of this research contract is to conduct an investigation of photopolymerization techniques and their utilization as a dry picture taking and printing medium for military use. Detailed requirements are contained in "Technical Guidelines for FR & C No. 62-ELS/R-2350 (61/2355)," dated 11 May 1961.

B. ABSTRACT

Polymerization of light-exposed areas of certain coated layers has been found to take place in the dry state. Effective formulations contained a light-sensitive ferric salt, a vinyl monomer and a cellulose derivative as binder. Development of the image took place during storage in an oven or darkroom, no peroxide being required. When the ferric salt of a phenolic alpha hydroxyacid was used, a colored image formed in the dry coating. Fixation was accomplished by washout. 3,4-Dihydroxymandelic acid partially reduced ferric ion in the dark (like catechol) and was also light sensitive with ferric ion (like mandelic acid). The ferric-3,4-dihydroxymandelic combination gave black resists on a dark background after exposure and peroxide immersion. Zinc oxide added to a formulation of the proper light sensitive ferric salt, monomer, and binder acted as a photoformer of hydrogen peroxide.

The synthesis of polymeric hydrazones was undertaken for investigation of their properties as substrates in the autoxidation photopolymerization system and as photoinitiators after conversion to the corresponding polymeric azohydroperoxides. Derivatives were prepared from oxidized polysaccharides, poly(methyl vinyl ketone-co-acrylamide) and a homopolymer of methyl vinyl ketone. The polyhydrazones derived from the latter two polymers readily underwent autoxidation; however, the product(s) were non-peroxidic and therefore useless as polymerization initiators. The polyhydrazones obtained from oxidized starch failed to undergo autoxidation and evidence was obtained that indicated the aldehyde function of the polymer acts as a built-in antioxidant. Three water-soluble derivatives of cumene have been prepared and evaluated as substrates for application in the photopolymerization system based on autoxidation. Of the three, only sodium p-isopropylbenzene sulfonate gave a positive result in solution experiments, and none was active in coated layers. The ability of allylic monomers to act as oxygen scavengers and comonomers in existing photopolymerization systems was investigated. Crotonylidene derivatives of polyvinyl alcohol were prepared and tested without success for activity in the iron-peroxide photopolymerization system. Due to incompatibility the effect of aromatic hydrazones on the iron-peroxide and ceric-oxalic systems could not be determined. Exploratory experiments have been conducted on a dry-process photopolymerization system based on the production of colored polymer from colorless monomer by virtue of the shift in unsaturation occurring when a 1,3-diene undergoes polymerization. A sample of 2,3-diphenylbutadiene was prepared and found not to polymerize in the presence of conventional initiators. Bromination gave a trans-1,4-dibromide and resulted in a bathochromic shift of approximately 15m μ .

C. PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

1. The following reports were issued:

- a. Monthly Report No. 7: "Investigation of the Photopolymerization Process"; 15 August - 15 September 1962; Authors: E. Cerwonka and F. W. Millard.
- b. Monthly Report No. 8: "Investigation of the Photopolymerization Process"; 15 September - 15 October 1962; Authors: E. Cerwonka and F. W. Millard.

2. A conference was held with Dr. Norman G. Gaylord, consultant on this contract, on 2 October 1962. Research progress was reviewed. A conference was also held at the U. S. Army Research and Development Laboratory on 31 August 1962 to review research progress. This meeting was attended by Dr. K. Leistner and Miss M. Levy. Dr. E. Cerwonka and Mr. S. Levinos represented Ansco.

D. FACTUAL DATA

1. Dry Photopolymerization Process

a. Colored Image Formed after Exposure

In a preceding report (August 1962 Quarterly Report) we have described formation of a greenish-black resist in exposed areas of certain photopolymerizable coated layers. Typically such a coating contains ferric ammonium sulfate, the ammonium salt of a phenolic alpha hydroxyacid, a monomer (acrylamide or MBA) and a binder, either hydroxyethyl cellulose or polyvinylpyrrolidone. A colored image appears during the hydrogen peroxide immersion step; fixation is achieved by washout of the unpolymerized areas.

It has since been found that an image similar in color can be formed in the dry coated layer by the process of (a) heating the exposed sample for 30 minutes or more in an oven at 50° or 73° C., or (b) storing the exposed sample in a dark room for a period of days.

Recipes of samples tested are listed in Table I.

Table I

	#0354 #0403 #0408	#0346	#0411	#0402
Natrosol 250L	0.625 g.	0.625 g.	0.625 g.	-
Polyvinyl- pyrrolidone	-	-	-	3.75 g.
N,N'-methylene- bisacrylamide	0.250 g.	-	0.250 g.	0.250 g.
Ferric ammonium sulfate dodeca- hydrate	0.700 g.	0.700 g.	0.700 g.	0.700 g.
m-hydroxymandelic acid	0.750 g.	0.750 g.	-	0.750 g.
m-hydroxyatro- lactic acid	-	-	0.825 g.	-
Ammonium hydroxide, 6N	0.75 ml	0.75 ml	0.75 ml	0.75 ml
Water, to	12.5 ml	12.5 ml	12.5 ml	12.5 ml

Binder and monomer were dissolved in a minimum volume of hot water (about 5 ml). Next the ammonium salt of the organic acid was dissolved in about 3 ml water and stirred in. These operations were carried out in white light. The iron salt was dissolved in water (about 2 ml), mixed in red light with the rest of the solution, and sufficient water was added to make

the total volume indicated. Finally, the solution was filtered in red light, coated on baryta paper, and allowed to dry.

A test strip of formulation #0411 was exposed 60 seconds to the light from a 375-watt reflector lamp at 16 inches, then suspended in an oven at 73° C. After a period of 30 minutes, a black image had appeared in the exposed areas. Further heating caused some darkening of the unexposed areas. When the sample was placed in a 50° oven, one hour or more was required to make the image visible. The background areas, however, were not appreciably darkened in the 50° oven, remaining a yellow or buff color.

When the exposure was reduced to 30 seconds, a visible image was observed in the 73° oven after two hours and in the 50° oven after about four hours.

Samples of coatings #0408 and #0346 were tested in the same manner. Exposures of 60 seconds followed by heating in the 73° oven gave an image in one to two hours. Heating in the 50° oven produced an image after four hours which became more pronounced overnight. There was less darkening of the unexposed areas of samples heated in the 50° oven. Reduction to 30 seconds of the exposures of #0346 and #0408 gave letter images which were too faint to be legible.

Heating of samples #0411, #0408 and #0346 in an oven at 110° C. after 30 seconds' exposure effected image formation with excessive discoloration of the unexposed areas within a period of 30 minutes.

Test samples of #0402 were also exposed for sixty seconds (usual light source), then heated. A faint but distinct image appeared in the sample in the 73° oven after two hours; none was visible, however, in the sample heated in the 50° oven. An exposed sample of #0402 placed in an oven at 110° C. also showed an image in two hours.

Test strips of a formulation (#0410) containing Natrosol 250"L" (2.5 g.), MBA (1 g.), ferric ammonium oxalate (2.47 g.) and water (to 50 ml) were exposed for 30 seconds and 60 seconds (usual light source). Close inspection revealed a faint print-out image after the 60-second exposure. This effect had been noted before in the case of long-exposed ferric ammonium oxalate coatings. Heating of samples in the 50° and 73° ovens for several hours tended to make the image disappear.

Exposed samples of #0411, #0408, #0346 and #0402 were stored at room temperature in the darkroom during the period other samples were being heated. There was no visible image formation during this period of hours.

Fixation of these colored images was accomplished by washout, which showed a metallic colored resist. No resist was obtained, however, when PVP was used as binder (#0402). Samples subjected to long heating had a deeper color after washout. When the exposed, heated samples were allowed to remain in room light, gradual darkening of the background areas became apparent. A dry fixation process, while desirable, has not yet been found.

Storage in the darkroom of exposed photopolymerizable coatings of this series was found to effect the formation of a colored photoresist. Generally several days' storage was required although the effect was somewhat accelerated by the passage of oxygen over the surface of the test strip. Several of the tests are described.

A sample of #0354 was exposed 30 seconds to the light from a 375-watt reflector lamp at 16 inches. No perceptible change had taken place during exposure, but a black image appeared in the exposed areas during a four-day period of cold storage (30°-40° F.) following the exposure. Samples given longer exposures showed a more dense image during the same storage period. Another sample having this composition (#0403) was exposed three minutes (same light source), then allowed to come in contact with a stream of moist oxygen (water bubbler) in the darkroom. Under these conditions a black image developed within three hours. Shortening of the exposure from three minutes to one minute required overnight storage subsequent to oxygen passage for a four-hour period. Dry oxygen did not produce an image in six hours; in this instance, the oxygen was bubbled through "Aroclor" (Monsanto's polychlorinated polyphenol) instead of water, the same rate of gas passage being maintained (two bubbles per second).

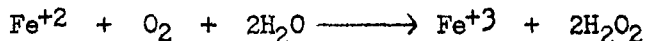
A sample of #0411 was exposed 60 seconds to the light from a 375-watt reflector lamp at 16 inches. After storage in the darkroom for three days, a black image appeared in the exposed areas. Washout of the sample showed the image to be a resist with a metallic luster.

Test results indicate that the presence of monomer has little, if any, effect on the rate at which the image is formed during storage. Exposure of a sample of #0346 for 60 seconds followed by heat development for one to two hours at 73° C. produced a visible image as did similar treatment of #0408. Storage at room temperature of both samples after exposure for 60 seconds brought out a black image in three days. When the strips were washed in warm water, a black image remained in both samples. For #0346 the image appears to consist of a pigment with an affinity for paper (monomer being absent). It had been expected that the production of colored matter would be more efficient in the absence of monomer.

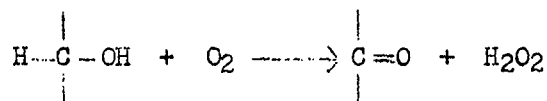
In a comparison of binders, appearance of the image was observed to be delayed when PVP was substituted for Natrosol, especially when exposed samples were stored at room temperature. Moreover, PVP-bound coatings showed no resist after washout. Exposure of a sample of #0402 for three minutes required four days' storage to yield an image. With shorter exposures (30 seconds or 60 seconds), no image had appeared after two weeks. Exposure of a sample of # 0354 (Natrosol) for 60 seconds gave an image with three days' storage.

Gelatin has not been compared with the other binders in this series of tests. Previously we have found it to be hardened or tanned by solutions of ferric ammonium sulfate. A large excess of ammonium mandelate (18 moles to one mole ferric ion) is still inadequate to liquefy the mass so that it can be coated. This undesirable effect does not take place when Natrosol or polyvinylpyrrolidone is substituted for gelatin.

The compound responsible for color observed in these tests is probably similar in structure to that obtained by mixing aqueous solutions of ferric ammonium sulfate and catechol. A black, water-insoluble precipitate is obtained which can be filtered and washed. The mole ratio of catechol to ferric ion may be 1/3:1, 1:1, or 3:1. Weinland⁽¹⁾ has identified this and similar complexes as consisting simply of ferric ion and catechol or a derivative of catechol. In explaining the formation of a colored image in the coating during storage at room temperature or in an oven, we postulate the gradual formation of a ferric-catechol complex. Photoformed ferrous is oxidized by atmospheric oxygen to the ferric state. Traces of hydrogen peroxide may be formed at the site of the photoproduct ferrous ion as follows:



As discussed by Yost and Russell⁽²⁾ ferrous and other metal ions may reduce oxygen with or without formation of an intermediate peroxide stage. Hydrogen peroxide so formed can react with ferrous ion to liberate hydroxyl radicals. Entry of one hydroxyl group into a ring position ortho to the phenolic hydroxyl of the acid effects the formation of a ferric-catechol complex. It is not yet clear whether hydroxyethyl cellulose enters into the color producing reaction. At elevated temperatures it is known that the carbinol groups of secondary alcohols are oxidized to carbonyl with accompanying formation of hydrogen peroxide^(3a).



b. Uncolored Resist Formed after Exposure

A formulation on paper base that consists of a light sensitive ferric salt, monomer, and binder generally requires peroxide treatment after exposure to give a resist. When the ferric salt is derived from a phenolic alpha hydroxyacid, the resist is colored as was described in Section 1, a. We have recently determined that coating formulations consisting of ferric ammonium sulfate, the ammonium salt of an alpha hydroxyacid, monomer, and hydroxyethyl or carboxymethyl cellulose as binder, exposed, then stored for an appropriate period will show a resist after washout (no peroxide required).

A recipe (#0410, quantities given in Section 1, a) coated on paper base was exposed to the light from a 375-watt lamp at 16 inches for a period of 30 seconds. When subjected to an immediate water wash, no resist was found, as expected. When, however, the exposed sample was stored five minutes in the dark, then washed, a resist appeared. Exposure for ten seconds, storage for 50 minutes, followed by washout gave a resist. Exposure for five seconds followed by overnight storage (15 hours) before washout gave a resist. Minimum exposure required to produce a resist was three seconds, yielding a resist after overnight storage followed by washout. Reducing the exposure still further did not give a resist, regardless of the duration of the storage period. Using the same test coating (#0410), an exposure of one second followed by peroxide immersion and water wash was sufficient to give a resist. Hence it appears that more ferrous ions are required to yield a resist by the method of exposure followed by storage than by the method of exposure followed by peroxide immersion.

A formulation (#0409) comprising ferric ammonium sulfate (2.88 g.), mandelic acid (2.74 g.), ammonium hydroxide, 6N (3.0 ml), Natrosol (2.5 g.), MBA (1.0 g.) and water (to 50 ml) required overnight storage (15 hours) after 30 seconds' exposure to yield a resist. Exposure of the same sample for one second followed by peroxide immersion gave a resist immediately. In another comparison test, two strips of #0409 were exposed, one minute each, under a $\sqrt{2}$ step wedge. One strip was immersed in hydrogen peroxide (1%) and washed. The other was stored in the darkroom for a period of one week, then washed. Inspection showed that polymer on the peroxide-treated sample extended to the 1.72 (optical density) step, corresponding to a minimum exposure of 1.1 seconds. Polymer on the stored sample extended only to the 0.28 (optical density) step, corresponding to an exposure of 31 seconds. These data indicate that about 30 times more ferrous ion is required to produce a resist by dry storage than by peroxide when mandelic acid is used to complex the iron. When oxalic acid was used (#0410), about three times more ferrous ion was needed. The

assumption is made that photoformed ferrous concentration is directly proportional to exposure. Overnight storage of an exposed coating containing citric acid (#0358) in place of oxalic or mandelic showed that there also imagewise polymerization took place, as shown by washout. The photoreduction product of ferric mandelate is benzaldehyde⁽⁴⁾; that of ferric citrate is acetone; and that of ferric oxalate is carbon dioxide. Hence ferric mandelate yields an autoxidizable compound--benzaldehyde--which might use up ferrous ion more rapidly (through its percompound oxidation intermediate) than the other organic photoreduction products.

Carboxymethyl cellulose was substituted for hydroxyethyl cellulose in two coating formulations. #0476 contained CMC (1.0 g.), MBA (1.0 g.), ferric ammonium oxalate (2.47 g.) and water (to 50 ml). #0477 contained 0.5 g. CMC but was otherwise identical to #0476. Exposure of samples for 30 seconds each followed by overnight storage and subsequent washout gave resist images.

When other binders were substituted for the cellulose derivatives and the same exposures were made, no resist was obtained. Washout followed storage periods that were equivalent to or longer than those used for hydroxyethyl cellulose coatings. Polyvinylpyrrolidone, 15 g., was substituted for Natrosol in the recipe for #0410 to give formulation #0412. #0413 contained PVP along with monomer, ferric ammonium sulfate, ammonium hydroxide and mandelic acid in the quantities listed for #0409. Gelatin (Atlantic #10299), 5.0 g., was used as binder in #0414, which contained ferric ammonium oxalate and MBA in the quantity used in #0409. Ferric ammonium sulfate (2.88 g.), citric acid (3.46 g.) and 6N ammonium hydroxide (9.0 ml) were added to gelatin (5.0 g.) and MBA (1.0 g.) to make up #0415. Exposures were made of samples of these four coatings (#0412, #0413, #0414 and #0415) for periods of five seconds and also 30 seconds. The samples were stored overnight and for periods up to one week. No resist was apparent after washout of any of these samples. Moreover, no resist was evident after peroxide immersion and washout of these stored samples. The photoproduced ferrous ion had evidently been reoxidized by a different path in PVP or gelatin coatings than that followed in the cellulose derivative coatings. For the cellulose derivatives, we may postulate the formation of hydrogen peroxide at the site of photoformed ferrous ion. Possible reactions involved could be those listed in Section 1,a for the case of the colored resist--oxidation of carbinol linkages accompanying oxidation of ferrous ion.

To compare the effect, if any, of binders on the reoxidation of photoformed ferrous ion, we assayed samples of #0412 (PVP), #0414 (gelatin) and #0448 (Natrosol--same recipe as #0410) after exposure and storage. Table II lists the colorimeter readings; in parentheses these have been translated into milligrams ferrous ion per exposed disc. Data are plotted in Graph I.

Table II

<u>Colorimetric* Assay of Ferrous Concentration</u>							
<u>Binder</u>	<u>Coating #</u>	<u>Sample Unexposed</u>	<u>Samples Exposed Ten Minutes, then Stored</u>				
			<u>0 day</u>	<u>1 day</u>	<u>2 days</u>	<u>3 days</u>	<u>4 days</u>
Polyvinylpyrrolidone	0412	2.5 (.003)	89 (.068)	30 (.023)	14 (.011)	9.5 (.008)	9 (.008)
Gelatin (Atlantic)	0414	3 (.003)	133 (.102)	72 (.054)	48.5 (.038)	45 (.034)	36 (.028)
Hydroxyethyl cellulose	0448	2 (.002)	80.5 (.062)	13 (.010)	8 (.007)	8 (.007)	7 (.006)

*The colorimetric reading of a blank (reading "2") has been subtracted from all tabulated readings.

Experimental: Discs measuring 3.434 square centimeters in area were cut out of the test strips by means of a punch. These samples were exposed ten minutes at 16 inches to the light from a 375-watt reflector lamp. One pair of discs from each of the three samples was then assayed for ferrous ion immediately. The other pairs were assayed after the number of days indicated in Table II. "Zero day" indicates the assay was made immediately after exposure. The ferrous colorimetric reading depends on the transmissivity of a ferrous-phenanthroline complex. Each disc is immersed in a 100 ml volumetric flask containing 5 ml of 0.1% phenanthroline and 1.0 ml of .05N hydrochloric acid, water being added to make 100 ml. The procedure was described in our December 1959 Quarterly Report (Table III of that report lists assay data then obtained on the aerial reoxidation of ferrous ion in a ferric ammonium citrate coating.)

Discussion of Graph I: The data suggest that ferrous ion is reoxidized at a slightly different rate in each binder. This rate may depend on the total surface area exposed by each formulation on the paper support. Whereas photoformed ferrous was reoxidized in each coating, different pathways of oxidation are possible in each binder, as has been suggested.

We have made the assumption that the mode of reoxidation is the same for short and long exposures. Assay of ferrous by our method when applied to samples exposed for a few seconds gave relatively low colorimetric readings. A relatively greater reading error is thereby introduced. The following data were obtained, however, as shown in Table III.

Table III

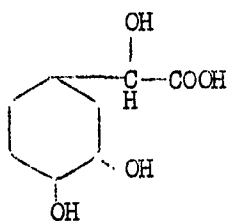
<u>Coating #</u>	<u>Time of Reading</u>	<u>Colorimeter*</u>	<u>Mg Ferrous per Disc</u>
0448	Unexposed	2	.002 (not photoproduced)
0448	Exposed 30 seconds	6.5	.006
0448	Exposed 30 seconds, then stored 15 hours	2	.002

*The colorimetric reading of a blank (reading "2") has been subtracted from the tabulated readings.

c. Colored Resist to Be Formed during Exposure

The formation of a colored washout-resistant image during exposures of a few seconds has remained an objective during the past quarter. Data presented in our previous Quarterly Report suggest that a formulation comprising ferric ion, ammonium meta-hydroxy atrolactate, monomer, and hydrogen peroxide should be dark stable. A ratio of 6:1 or greater of hydroxyacid to ferric ion may be required. The yield of this acid (not previously reported) thus far realized has been a fraction of one percent based on meta hydroxyacetophenone. Not enough of the material has been prepared to date to make a suitable composition including hydrogen peroxide. One composition (#0411) incorporating the new acid was described in Section 1, a.

2. Properties of Ferric 3,4 Dihydroxymandelate



The preparation of 3,4-dihydroxymandelic acid was carried out by the method of Shaw, et al,⁽⁵⁾. Starting with 3,4-dihydroxybenzaldehyde we obtained as product a tan-colored solid melting at 136° C. Mixing with ferric ammonium sulfate in the ratio of 3 moles acid to 1 mole ferric ion gave the curve shown in Graph II. The absorption toward the blue end of the spectrum is characteristic of that of ferric alpha hydroxy acids. The absorption in the red portion of the spectrum is probably due to the ferric-catechol type of complex for which the hydroxyls at positions 3 and 4 are responsible.

While the ferric salt of this acid is indeed sensitive to visible light, some chemical or dark reduction of ferric to ferrous is effected by the acid acting as a catechol derivative. Weinland's studies of ferric-catechol complexes⁽¹⁾ make no mention of the reducing action of catechol on ferric compounds that has been reported in more recent investigations^(6,7).

Formulations prepared thus far with this acid are listed in Table IV.

Table IV

	<u>0481</u>	<u>0482</u>
Natrosol 250"L"	0.313 g.	0.313 g.
MBA	0.125 g.	0.125 g.
3,4 Dihydroxymandelic acid	0.414 g.	0.138 g.
Ammonium hydroxide, 6N	0.375 ml	0.125 ml
Ferric ammonium sulfate dodecahydrate	0.362 g.	0.362 g.
Water, to	6.5 ml	6.5 ml

The formulations were prepared and coated on paper base in the same manner as those listed in Table I. Filtering of the solution in red light was omitted, however.

Exposure for 60 seconds of these coatings to the light from a 375-watt lamp at 16 inches followed by hydrogen peroxide immersion and washout yielded a black resist which was superimposed on a background layer of polymer. The background layer is undoubtedly due to the reducing action of the acid acting as a catechol and producing ferrous ion. This ferrous is superimposed on that which is photoformed by the acid acting as a mandelic acid derivative.

Additional formulations involving this acid are planned with the objective of producing a color in the dry state by the action of atmospheric oxygen. Test solutions of ferrous ammonium sulfate mixed with 3,4-dihydroxymandelic acid have been found to assume a dark green color within hours. It may be necessary to combine oxalic or citric acid with 3,4-dihydroxymandelic acid to achieve the effect of a colorless unexposed layer, darkening in the exposed areas by the subsequent action of oxygen.

3. Zinc Oxide as a Photochemical Source of Hydrogen Peroxide

Zinc oxide has been employed by us in several tests in order to photo-produce hydrogen peroxide. In the presence of the ferric salt of a phenolic alpha hydroxyacid a black print-out image should result.

The chief difficulty encountered has been the incompatibility of zinc oxide with ferric ammonium sulfate-ammonium mandelate in Natrosol. Extremely viscous solutions are the result. Our color-forming acids are derivatives of mandelic acid and would not be expected to behave differently.

The following formulation (#0439) was prepared and coated on baryta paper:

Natrosol 250"L"	2.5 g.
MBA	1.0 g.
Zinc Oxide, "Green Seal" (New Jersey Zinc Company)	1.0 g.
Ferric ammonium citrate, brown, 36 g/100 ml aq.	5.0 ml
Water, to	50 ml

Exposures of 30 seconds to the light from a 375-watt reflector lamp at 16 inches followed immediately by a water wash gave a white resist. When the concentration of zinc oxide was increased to 2.0 grams (#0441) or reduced to 0.5 gram (#0438) or when no zinc oxide was present (#0440), no resist appeared after exposure and washout. No resist was obtained from a formulation (#0423) containing ferric ammonium oxalate (2.47 g.) and zinc oxide (0.5 g.), otherwise the same as #0439. When 1 gram zinc oxide was mixed with ferric ammonium oxalate, MBA, and Natrosol (#0443), a viscous solution was obtained which coated poorly. No resist was obtained after exposure and washout of #0443. Recipes (#0424, #0442) containing ferric ammonium sulfate, ammonium mandelate, monomer and zinc oxide (0.5, 1.0 g.) were likewise extremely viscous. Coatings gave no resist image.

The positive results obtained with #0439 would indicate the photo-formation of hydrogen peroxide on the surface of zinc oxide. Polyvinylpyrrolidone (15 g.) was substituted for Natrosol in coating #0451. The recipe was otherwise the same as that of #0439. Exposures of samples of #0451 for periods of 30 seconds and 60 seconds followed by washout gave no resist. We have not yet tested gelatin as a binder for combinations of zinc oxide, ferric salt and monomer.

4. Reduction of Oxygen to Hydrogen Peroxide in Solution Tests

In Sections 1, a and 1, b evidence was presented indicating a relatively slow reduction of oxygen to hydrogen peroxide in coated layers. Photopolymerizable mixtures having either hydroxyethyl cellulose or carboxymethyl cellulose as binder show a resist when aged or heated in the presence of photoformed ferrous ion and monomer. Presumably the binder takes part in the reaction, since coatings containing polyvinylpyrrolidone or gelatin did not give the result. An effort was made to simulate the reaction in aqueous

solution, no binder being involved. A stock solution was prepared from ferric ammonium sulfate (197 mg.) and oxalic acid (111 mg. - anhydrous) in 100 ml deionized water. The following experiments were carried out:

- (a) Into a solution consisting of A-5, 5.0 ml, and ferric ammonium sulfate-oxalic acid (described above), 1.0 ml, there was passed in red light nitrogen for 10 minutes, oxygen for 5 minutes, and nitrogen for an additional 10 minutes in the sequence named. No reaction occurred. The purpose of alternate nitrogen and oxygen passage was the removal of traces of volatile material and carbon dioxide, along with the oxidation of any extraneous ferrous ion.
- (b) The solution from (a) was now exposed with stirring to the light from a 1000-watt tungsten lamp at 23 cm. A gel or polymer formed in one minute 12 seconds. In this experiment polymerization could have been initiated by any of several photoformed radicals such as the oxalate radical ion. Several investigators postulate the decomposition of ferric ammonium oxalate into particles such as the oxalate radical ion by the action of ultraviolet light⁽¹⁰⁾. Polymerization could also have been effected in (b) by the interaction of photoformed ferrous ion and traces of hydrogen peroxide. The hydrogen peroxide could result from reduction of aerial oxygen by ferrous ion.
- (c) A solution consisting of A-5, 5.0 ml, and ferric ammonium sulfate-oxalic acid solution, 1.0 ml, was treated as in (a). It was then exposed for two minutes with stirring to the light from a 1000-watt tungsten lamp at 23 cm. No reaction had taken place at this time. Nitrogen was now bubbled into the solution (red light). After one minute 27 seconds, the solution gelled.

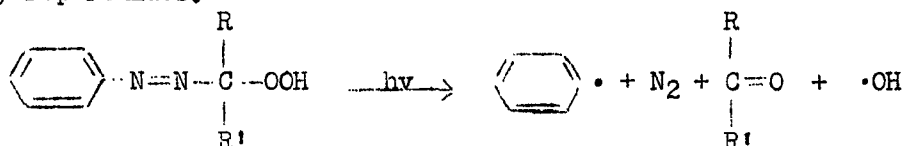
This experiment resembles somewhat the effect observed with resist formation in stored paper-base coatings. During the period of nitrogen passage, photoformed ferrous was being reoxidized by traces of ambient oxygen. Excess oxygen was flushed out by nitrogen, making more effective the action of the few molecules of hydrogen peroxide, believed to be formed by reduction of molecular oxygen.

- (d) A solution of ferric ammonium oxalate (175 mg./100 ml) was exposed five minutes with stirring to the light from a 1000-watt tungsten lamp at 23 cm. A sample was taken immediately and shaken with titanous sulfate in amyl alcohol. Yellow titanous ion formation is a specific test for hydrogen peroxide^(3b). The test was negative.

Although no hydrogen peroxide was detected by this test, there is the possibility that hydrogen peroxide is formed and reacts with excess ferrous ion as fast as it is formed from molecular oxygen. If this is the case, hydroxyl radicals could be present.
$$(\text{Fe}^{+2} + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}^{+3} + \cdot\text{OH} + \text{OH}^-)$$
 Hydroxyl radicals are not necessarily detected by the titanous sulfate test, which is specific for molecular hydrogen peroxide.

5. Polymeric Azohydroperoxides

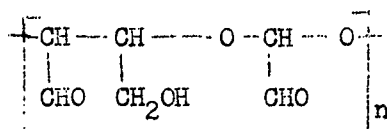
As previously reported, the azohydroperoxides obtained by autoxidation of aliphatic phenylhydrazones are colored compounds and are useful blue sensitive photoinitiators of vinyl polymerization. Stoltzenberg⁽¹¹⁾ first discovered this property and proposed the following reaction to account for the formation of free radicals on photodecomposition of azohydroperoxides.



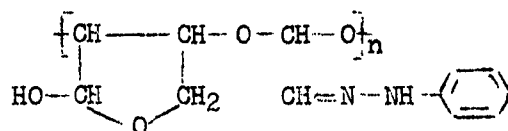
The preparation of a polymeric phenylhydrazone has been undertaken to explore its properties both as an autoxidation substrate and as a polymeric photoinitiator after conversion to the corresponding azohydroperoxide. Previously, a terpolymer of methyl vinyl ketone, acrylamide and acrylic acid was prepared according to the procedure disclosed in U. S. Patent 2,632,704 relating to the preparation of gelatin substitutes for use in photographic emulsions. The polymer was soluble in 70% ethanol and was converted to the polymeric hydrazone by reaction with phenylhydrazine. Oxidation of an alcoholic solution of the polyhydrazone failed to give a peroxidic polymer.

Subsequent to these experiments, it was learned that Busch and Kunder⁽¹²⁾ reported that the autoxidation of aromatic hydrazones in aqueous or alcoholic solution leads to non-peroxidic products. Inasmuch as the methyl vinyl ketone, acrylamide, acrylic acid terpolymer hydrazone derivative was insoluble in hydrocarbon solvents, this may explain why it could not be converted to the polymeric azohydroperoxide.

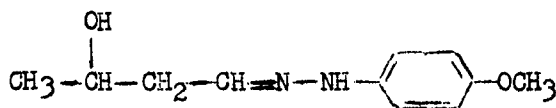
Barry and Mitchell⁽¹³⁾ have reported the preparation of polymeric hydrazones by the treatment of oxidized polysaccharides with aromatic hydrazines. Oxidized polysaccharides are commercially available from the Miles Chemical Company under the trade name "Sumstars." These polymers have the following unit structure:



Treatment of a 10% aqueous solution of Sumstar-S (91% oxidized to the dialdehyde form) with a solution of phenylhydrazine in 10% acetic acid gave a bright yellow solid, insoluble in water, soluble in alcohol, benzene and ether. Mester⁽¹⁴⁾ has shown the hydrazones of similar oxidized polysaccharides to have the following hemiacetal structure:



The polyhydrazone was purified by precipitation from alcoholic solution with water and dried in vacuo. No oxygen absorption was observed when a benzene solution of the polyhydrazone was stirred in an atmosphere of oxygen supplied by a gas burette. Previously it was found that the presence of an electron donating group such as p-OCH₃ in the phenylhydrazine nucleus strongly accelerated the rate of autoxidation of the corresponding acetone derivative. Accordingly, a sample of Sumstar-S was reacted with p-methoxyphenylhydrazine and the resulting orange colored polyhydrazone exposed to oxygen in benzene solution. Again no oxygen absorption took place. As a model experiment, a sample of aldol p-methoxyphenylhydrazine was prepared and found to undergo a rapid autoxidation in benzene solution.



aldol p-methoxyphenylhydrazine

Unexpectedly, the product(s) of this autoxidation did not appear to be peroxidic inasmuch as they did not initiate polymerization of A-5 solution either in combination with ferrous ion or on exposure to light. It was therefore concluded that the presence of a hydroxyl group in the hydrazone molecule does not preclude its susceptibility to autoxidation; however, it may alter the nature of the product(s) obtained.

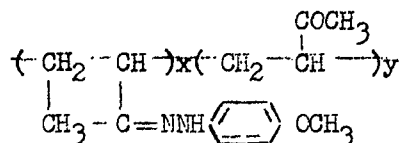
The infrared spectrum of the polymeric hydrazone indicated the presence of some unreacted aldehyde groups which could conceivably inhibit the autoxidation reaction by chain transfer at the formyl hydrogen. To check this possibility, the rate of oxygen absorption of a 0.02M solution of acetone-p-bromophenylhydrazine was determined in the presence and absence of Sumstar-S. The presence of the dialdehyde starch reduced the rate of oxygen absorption from 2.0 ml O₂/min. to 1.1 ml O₂/min., indicating a strong retardation presumably due to the aldehyde content. A fresh sample of polyhydrazone was prepared by adding the Sumstar-S solution to a two-fold excess of p-methoxyphenylhydrazine in an effort to insure complete conversion of the aldehyde groups to hydrazone. The infrared spectrum of this sample indicated only a very slight carbonyl absorption at 5.85μ. However, again a benzene solution failed to absorb oxygen.

At this point, experimentation with hydrazones derived from the Sumstar polymers was discontinued, and the preparation of polymers derived from methyl vinyl ketone was undertaken. Initially, vinyl acetate was polymerized in the presence of 10 and 50 mol % of methyl vinyl ketone by a standard emulsion technique⁽¹⁵⁾, employing a benzoyl peroxide, ferrous ammonium sulfate-sodium pyrophosphate initiator system. Very low conversions were obtained, and the polymer appeared to be of very low molecular weight. However, when acrylamide was used as the comonomer in place of vinyl acetate, good conversions of a tractable copolymer were obtained. The following procedure gave a copolymer analyzing for 9.5% nitrogen indicating a molar ratio of 1:1.1 acrylamide to methyl vinyl ketone.

Poly(methyl vinyl ketone-co-acrylamide). In a flask provided with a stirrer, reflux condenser, and nitrogen atmosphere was placed 40 g. (0.56 mole) of freshly distilled methyl vinyl ketone, 40 g. (0.06 mole) of acrylamide, 500 ml of deionized water, and 10 ml of isopropanol. After warming to 70°, 0.2 g. of potassium persulfate was added and the temperature maintained at 70° for one hour. The polymer was isolated from the viscous reaction mixture by pouring into a large excess of isopropanol agitated in a Waring Blender. After drying in vacuum, a white, granular copolymer was obtained.

Conversion to the p-methoxyphenylhydrazone was effected by treating a dispersion of the copolymer in 10% acetic acid with a calculated equivalent of p-methoxyphenylhydrazine. The reaction was conducted in an atmosphere of nitrogen, and the orange polymeric hydrazone was stored in vacuo prior to oxidation. Autoxidation was carried out by stirring a fine suspension of the copolymer in benzene in an oxygen atmosphere provided by a gas burette. Within one hour, 36% of the calculated amount of oxygen was absorbed, and the polyhydrazone had become dark brown in color. Attempts to initiate the polymerization of A-5 solution by exposure to light in the presence of the polyhydrazone and in conjunction with ferrous ion failed. The non-peroxidic nature of the oxidized polyhydrazone was further confirmed by its failure to liberate iodine from acidified potassium iodide solution.

In a similar manner a sample of poly(methyl vinyl ketone) obtained by the thermal polymerization of freshly distilled monomer was derivatized with p-methoxyphenylhydrazine in dioxane solution. The yellow polyhydrazone was soluble in dioxane from which it could be precipitated by the addition of water. Nitrogen analysis indicated that approximately one in every ten monomer units had been converted to hydrazone.



where $y = 10x$

As in the case of the polyhydrazone derived from poly(methyl vinyl ketone-co-acrylamide) a suspension of the polyhydrazone in benzene rapidly absorbed oxygen; however, again the oxidized polymer was non-peroxidic and accordingly useless as a polymerization initiator. No satisfactory explanation for the failure of the polymeric p-methoxyphenylhydrazones to yield azohydroperoxides on oxidation has been forthcoming from the investigation thus far, and further experimentation along these lines has been discontinued.

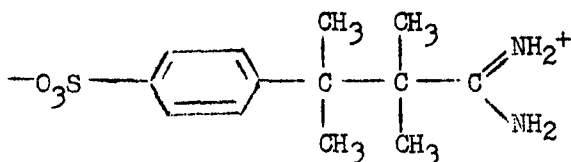
6. Photopolymerization Based on Autoxidation

a. Cumene Derivatives as Autoxidation Substrates

The previous Quarterly Report outlined the synthesis of three water-soluble cumene derivatives--sodium p-isopropylbenzene-sulfonate, p-cuminol, 2-(p-cuminoxy)-ethylamine--for evaluation as autoxidation substrates. It was hoped that exposure of these compounds in the presence of a suitable photosensitizer would result in a chain autoxidation with molecular oxygen, leading to a hydroperoxide end product. The hydroperoxide could then be utilized to initiate polymerization in conjunction with ferrous ion. Thus this system would be the reverse of the usual iron-peroxide photopolymerization system in that the exposure generates a hydroperoxide rather than a ferrous ion latent image. An increase in speed should result as a consequence of the amplification inherent in the chain autoxidation reaction.

Initially, 0.05M aqueous solutions of the three cumene derivatives were prepared and checked for dark reaction with molecular oxygen by stirring in a flask attached to a gas burette filled with oxygen. No significant oxygen absorption was observed for periods of 6-18 hours.

These experiments were repeated in the presence of light and rose bengal as the photosensitizer. After one hour the sodium p-isopropylbenzene sulfonate and the 2-(p-cuminoxy)-ethylamine absorbed 5 and 9 mol % of oxygen respectively. Conversely, p-cuminol failed to absorb any measurable amount of oxygen. Addition of the oxidized solution of sodium p-isopropylbenzene-sulfonate to an A-5 solution containing ferrous ion resulted in instantaneous polymerization. When the oxidation was carried out at 40° in the presence of 2,2'-azobisisobutyramidine dihydrochloride as a thermal source of free radicals, 9 mol % of oxygen was absorbed. On cooling, a non-peroxidic, crystalline solid melting at 136-137° separated from the reaction mixture. Elemental and infrared analysis indicate this compound to have the following structure:



This result was surprising in that it shows that an appreciable amount of the p-sulfonated cuminy radicals do not preferentially react with oxygen even in an oxygen-saturated environment.

Coatings were prepared containing sodium p-isopropylbenzene sulfonate and 2-(-p-cuminoxy)-ethylamine in conjunction with rose bengal and N,N'-methylene bisacrylamide in a polyvinylpyrrolidone binder. Long exposures to tungsten light followed by processing in 1% ferrous ammonium sulfate failed to produce any polymerization.

7. Effect of Allylic Derivatives on Photopolymerization

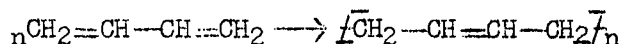
a. Polyvinyl Alcohol Acetals

As outlined in the previous Quarterly Report, several batches of polyvinyl alcohol (Elvanol 51-05) were acetalized with crotonaldehyde to provide an allylic substituted polymer for trial as an oxygen scavenger in the iron-peroxide photopolymerization system. Trial coatings were prepared containing polyvinyl alcohol modified with 0.125 and 0.25 equivalents of crotonaldehyde in addition to the standard ferric ammonium citrate, N,N'-methylenebisacrylamide formulation. Comparison of these coatings with control coatings containing no acetalized polyvinyl alcohol showed the modified coatings to be slower in speed. The loss in speed appeared to be associated more with a decrease in adhesion induced by the modified polyvinyl alcohol, rather than an increase in inhibition period.

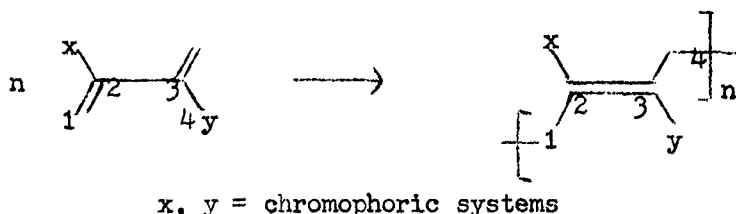
8. Dry Process Photopolymerization

The most obvious approaches to dry process photographic materials entail either direct print-out systems or the use of thermal, radiant, electrical or magnetic energy for post-development of a latent image. One approach to a print-out system based on photopolymerization depends on photoconversion of colorless monomer to colored polymer or, conversely, colored monomer to colorless polymer. Vinyl polymerization is accompanied by a loss in unsaturation and, since unsaturation is essential for light absorption, it is difficult to envisage a direct conversion of vinyl monomer to saturated polymer that would result in color formation. However, one possible solution to this problem embodies the following principles: The free radical initiated polymerization of 1,3-dienes is well known, and in general

proceeds chiefly by 1,4-addition leading to polyunsaturated polymers. For example, the radical initiated polymerization of butadiene leads to an elastomer in which 70-80% of the monomer segments are joined in the 1,4- manner.



The concomitant conversion of a single bond to a double bond between carbons 2 and 3 could be utilized to bring two chromophoric groups into conjugation as illustrated by the following general scheme:

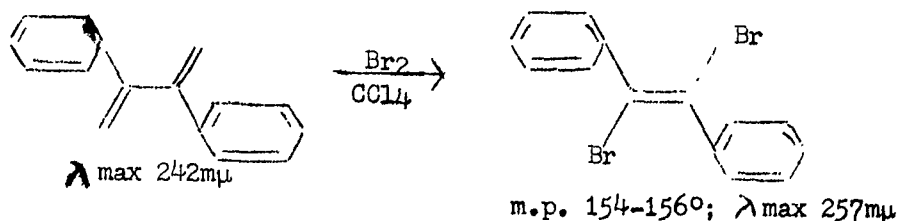


This increase in conjugation would be expected to result in a strong bathochromic shift which, with the appropriate selection of chromophoric systems could result in the formation of colored polymer from colorless monomer.

As a starting point for the exploration of this proposal, a sample of 2,3-diphenylbutadiene was prepared by the dehydration of acetophenone pinacol with fused potassium bisulfate according to the procedure described by Alder⁽¹⁶⁾.

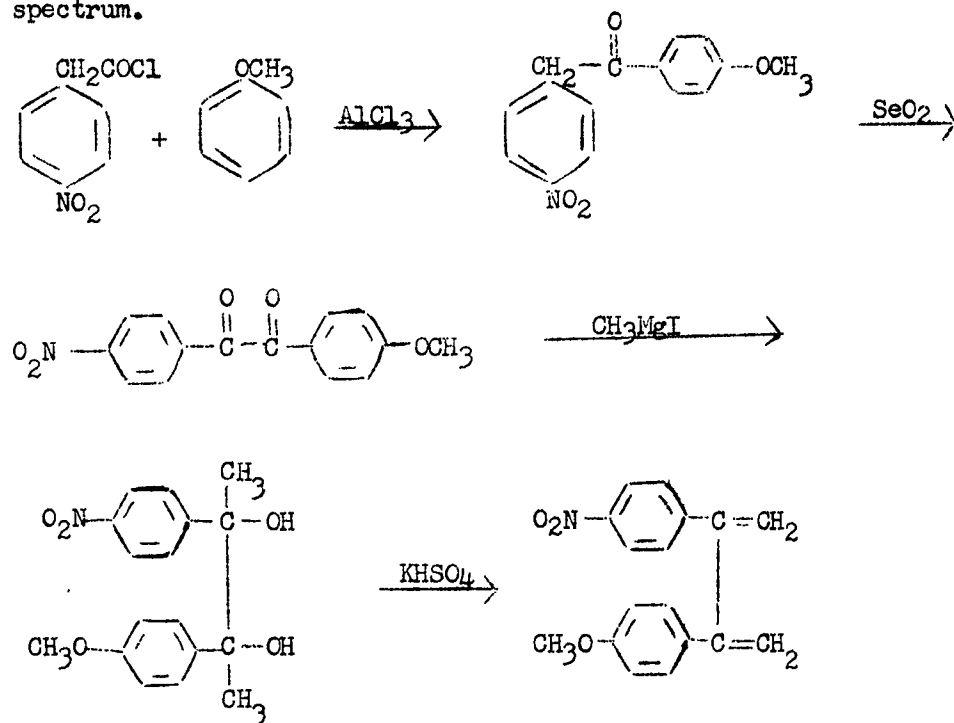
Diphenylbutadiene is a colorless solid melting at 48-50° C. and was found to undergo decomposition when stored in air, resulting in the formation of a yellow oil which has not been identified. The ready solubility of the decomposition product in several organic solvents indicated that it is not polymeric in nature.

Several attempts to polymerize 2,3-diphenylbutadiene in sealed ampoules using 2,2'-azobisisobutyronitrile and benzoyl peroxide as thermal initiators gave no indication of polymerization. In both cases unchanged monomer was recovered after heating at 45-50° for 16 hours. Similarly, attempts to polymerize an alcoholic solution of the diene using ferrous ammonium sulfate and hydrogen peroxide as a redox initiator system failed to produce any polymer. At this point, recourse was taken to bromination to produce the desired shift in unsaturation.



Infrared analysis and a consideration of molecular models indicate the bromination product to have the trans-1,4-configuration. The bathochromic shift produced by increasing the conjugation of the system was surprisingly small, as can be seen from the $\lambda_{\max}$ values indicated in the equation above. Examination of a Hirschfielder model of 1,4-dibromo-2,3-diphenylbutene-2 shows that only the trans configuration is possible and that rotation of the phenyl rings is restricted to the point that coplanarity with the central ethylene bond cannot occur. The resulting steric inhibition of resonance doubtlessly is the cause of the small $\lambda_{\max}$. This is further supported by the fact that trans-stilbene, in which free rotation of the phenyl rings can occur, has $\lambda_{\max}$ 295m μ .

The synthesis of 2-(p-nitrophenyl)-3-(p-methoxyphenyl) butadiene-1,3 was undertaken according to the following synthetic scheme in an attempt to shift the absorption to the visible region of the spectrum.



The synthesis went smoothly up to the preparation of 4-nitro-4'-methoxybenzil. Addition of methyl magnesium iodide to this compound, however, appears to be complicated by interference from the nitro group. Currently a new synthetic route is being sought.

- References -

1. R. F. Weinland and K. Binder, Ber. 45, 148-54, 1113-24
2. "Systematic Inorganic Chemistry," D. M. Yost and H. Russell, Prentice-Hall, New York (1944), 261, 368-9
3. "Hydrogen Peroxide," W. C. Schumb et al (a) 89
(b) 549
4. A. Benrath, Ann. 382, 222 (1911)
5. K. N. F. Shaw, A. McMillan and M. D. Armstrong, J.Org.Chem. 23, 27-32 (1958)
6. J. H. Merz and W. A. Waters, J.Chem.Soc., 2427-33 (1949)
7. L. Cosgrove and W. A. Waters, J.Chem.Soc., 1726-30 (1951)
8. M. C. Markham, M. C. Hannan and S. W. Evans, J.Am.Chem.Soc. 76, 820 (1954)
9. M. C. Markham and K. J. Laidler, J.Phys.Chem. 57, 363 (1953)
10. "Photochemistry in the Liquid and Solid States," L. J. Heidt et al, 41-47, J. Wiley and Sons, New York (1960)
11. Stoltzenberg, Thesis, Technisch Hochschule, Karlsruhe (1958)
12. Busch and Kunder, Ber., 49, 2345 (1916)
13. Barry and Mitchell, J.Chem.Soc., 3631 (1953)
14. Mester, J.Am.Chem.Soc. 77, 5452 (1955)
15. Marvel, Deamen, Overberger & Kuhn, J.Poly.Sci., 3, 128 (1948)
16. Alder, Ann. 570, 212 (1950)

E. PROGRAM FOR NEXT INTERVAL

1. Methods of speeding up the dry photopolymerization process (Section 1) will be studied. Emphasis will be placed on means of reducing the time required for appearance of the colored image which is formed by the interaction of oxygen and photoproduced ferrous ion in the presence of a catechol-type compound. Formulations involving 3,4-dihydroxymandelic acid and other light-sensitive ferric salts will be prepared. Synthesis of 3,5-dihydroxymandelic acid (not reported) is to be carried out for use in formulations.
2. Additional binders related to cellulose and starch will be compared with hydroxyethyl and carboxymethyl cellulose as to their effect in the dry photopolymerization process described in Section 1.
3. Electrolytic experiments are to be carried out with the objective of reducing molecular oxygen to hydrogen peroxide on coated surfaces, if feasible.
4. Further experimentation on the dry-process system outlined in Section 8 of this report will be carried out. Initially, this will involve the synthesis of 2-(p-nitrophenyl)-3-(p-methoxyphenyl) butadiene-1,3 or, if this proves to be impractical, a similarly substituted butadiene derivative.
5. The study and experimental investigation of the photopolymerization system based on photoinitiated autoxidation will be continued.

F. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

Levinos, Steven

Project Manager

Education:

Polytechnic Institute of Brooklyn
Brooklyn, New York
B. S. in Chemistry 1937

Employment:

Co-owner, Smith Chemical Works,
Edgewater, New Jersey
1936-1938

Ansbacher-Siegle Corporation
Staten Island, New York
1938-1942 Research Chemist

National Bureau of Standards
Washington, D. C.
1942-1947 Research Chemist

Signal Corps Engineering Laboratories
Fort Monmouth, New Jersey
1948-1955 Chief, Photographic Branch

Photo & Repro Division
General Aniline & Film Corporation
Binghamton, New York
1956- Manager, New Fields and Contract Research

Research Fields:

Pigments, radiochemistry, photographic processes,
photopolymerization

Man Hours Devoted to this
Project (15 August 1962 -
14 November 1962)

17

Cerwonka, Edward

Research Specialist

Education:

Fordham University
Ph.D. 1952 Organic Chemistry

Employment:

U. S. Testing Company
Hoboken, New Jersey
1952-1953 Research Chemist

U. S. Testing Company
Boston, Massachusetts
1953-1954 Research Chemist

Metaelectro Corporation
Laurel, Maryland
1954-1957 Senior Research Chemist

AnSCO, Division of General Aniline & Film Corp.
Binghamton, New York
1957- Senior Research Chemist

Research Fields: Radio isotopes as tracers, synthesis of radio
active organic compounds, synthesis of organic
nitrogen compounds, polymer chemistry.

Man Hours Devoted to this
Project (15 August 1962 -
14 November 1962) 440

Millard, Frederick W. Research Specialist

Education: Michigan State University
East Lansing, Michigan
Ph.D. 1958 Organic Chemistry

Employment: Texas U. S. Chem.
1958-1960 Senior Research Chemist

AnSCO, a Division of General Aniline & Film Corp.
Binghamton, New York
1960- Senior Research Chemist

Research Fields: Polymerization, organic reaction mechanisms,
free radical reactions.

Man Hours Devoted to this
Project (15 August 1962 -
14 November 1962) 232

We draw on other members of our Research staff for occasional consulting services:

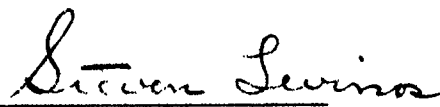
Dr. F. W. H. Mueller, Director of Research and Development

Dr. F. J. Kaszuba, Associate Director of Research and Development

Dr. H. F. Nitka, Associate Director of Research and Development

Dr. G. A. Wieseahn, Research Librarian

The Accounting Department Report on this Project will be submitted by the Federal Sales Department within 30 days.



Steven Levinos
Project Manager

HEADQUARTERS
U. S. ARMY ELECTRONICS RESEARCH AND DEVELOPMENT LABORATORY
FORT MONMOUTH, NEW JERSEY

SELRA/SL-SA

Contract No. DA36-039 SC-88933
Report No. Fourth Quarterly
Project Engineer: Marilyn Levy

DISTRIBUTION LIST

OASD (R&E), Room 3E1065 ATTN: Technical Library The Pentagon Washington 25, D. C. (1)	Commanding General U. S. Army Electronics R&D Activity ATTN: Technical Library Fort Huachuca, Arizona (1)
Chief of Research and Development OCS, Department of the Army Washington 25, D. C. (1)	Commander Armed Services Technical Info Agency ATTN: TIPCR Arlington Hall Station Arlington 12, Virginia (10)
Commanding General U. S. Army Electronics Command ATTN: AMSEL-RD Fort Monmouth, New Jersey (1)	Directorate of Research and Development Headquarters, USAF ATTN: AFDRD-SC Washington 25, D. C. (1)
Director U. S. Naval Research Laboratory ATTN: Code 2027 Washington 25, D. C. (1)	Chief, Bureau of Naval Weapons Photographic Division (FF PH-4) Department of the Navy Washington 25, D. C. (1)
Commanding Officer and Director U. S. Navy Electronics Laboratory San Diego 52, California (1)	Commanding Officer U. S. Naval Photo Center ATTN: Test & Evaluation Department U. S. Naval Air Station Anacostia, D. C. (2)
Commander Aeronautical Systems Division ATTN: ASARPL Wright-Patterson Air Force Base Ohio (2)	Signal Corps Liaison Officer Johns Hopkins University Operations Research Office 6935 Arlington Road Bethesda, Maryland Washington 14, D. C. (1)
Commander Air Force Cambridge Research Labs. ATTN: CRO L. G. Hanscom Field Bedford, Massachusetts (1)	Commanding General U. S. Army Intelligence Center ATTN: President USA Intelligence Board Fort Holabird Baltimore 19, Maryland (1)
Commander Rome Air Development Center ATTN: RAAD Griffiss Air Force Base New York (1)	

SELRA/SL-SA

DISTRIBUTION LIST FOR CONTRACT NO. DA36-039 SC-88933 (Continued)

Commander Aeronautical Systems Division Air Force Systems Command ATTN: ASD (ASRNRD-2) Wright-Patterson Air Force Base Ohio (1)	Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: SELRA/SL-LNR Fort Monmouth, New Jersey (1)
Technical Information Service U. S. Atomic Energy Commission P. O. Box 62 Oak Ridge, Tennessee (1)	Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: Logistics Division Fort Monmouth, New Jersey M/F SELRA/SL-SAP (Miss M. Levy) (15)
Chief U. S. Army Security Agency Arlington Hall Station Arlington 12, Virginia (2)	Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: SELRA/SL-DR Fort Monmouth, New Jersey (1)
Deputy President U. S. Army Security Agency Board Arlington Hall Station Arlington 12, Virginia (1)	Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: SELRA/SL-ADT Fort Monmouth, New Jersey (1)
Commanding Officer U. S. Army Electronics Materiel Command ATTN: SELFM/ES-ADJ Fort Monmouth, New Jersey (1)	Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: SELRA/SL-SA File Unit No. 1 Fort Monmouth, New Jersey (1)
Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: SELRA/SL-LNE Fort Monmouth, New Jersey (1)	Commanding Officer U. S. Army Electronics R&D Laboratory ATTN: SELRA/SL-TN Fort Monmouth, New Jersey (3)