# Investigation of Photopolymerization Process

## First Quarterly Report

14 FEBRUARY 1963 – 13 MAY 1963

Signal Corps Contract DA 36-039 AMC-00119-(E)
Order Number 5468-PM-63-91
PR & C Number 63-ELS/R-2350

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

Contractor
PHOTO AND REPRO DIVISION
GENERAL ANILINE & FILM CORPORATION
Binghamton, New York

General Aniline & Film Corporation
Photo and Repro Division
Binghamton, New York

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# "Investigation of the Photopolymerization Process"

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

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Project Manager: Steven Levinos

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

AD____________Accession No.____________

PHOTO & REPRO DIVISION, General Aniline & Film Corporation, Binghamton, New York
Investigation of the Photopolymerization Process
E. Cerwonka and F.W. Millard
First Quarterly Report, 14 February 1963 to 13 May 1963
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The ferric salt of 3,3′ dihydroxybenzilic acid initiates the polymerization of vinyl monomers in visible light without peroxide.

Uranyl acrylate and uranyl methacrylate yield opaque polymers when exposed to light. Solutions and coatings of these compounds are stable when stored in darkness.

Several methods of introducing color into a resist

Unclassified

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## A. PURPOSE

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

## B. ABSTRACT

One objective of the research program has been the elimination of hydrogen peroxide immersion as a processing step for photopolymerizable ferric salt coatings. In a continuation of work reported previously we find that the ferric salt of 3,3'-dihydroxybenzilic acid initiates the polymerization of vinyl monomers in visible light without peroxide. Coated layers of this ferric salt require shorter exposures when the photocatalyst concentration is relatively low.

The effectiveness of uranyl ion as an initiator of photopolymerization is under study. Uranyl acrylate and uranyl methacrylate yield opaque polymers in visible light. Solutions and coatings which are stable in the dark have been prepared.

Another objective of the program has consisted in the production of color in a photo image by the simplest possible means. A colored (green) print-out image results from the exposure of a coated layer containing ferric benzilate and the hydrochloride of the leuco base of thiophene green. 1,3-dihydroxy-1,3-dimethylglutaric acid has been synthesized; its ferric salt is light sensitive. The expected red-colored photodecomposition product of the ferric salt of this acid has not yet been observed in coated layers.

In continuation with our efforts to achieve a dry processable photographic system based on photopolymerization by the production of a colored photoresist, the synthesis of color former monomers related to N,N'-methylenebisacrylamide has been pursued. N,N'-(2-hydroxybenzylidene)-bisacrylamide was prepared and found to exhibit reactivity comparable to that of N,N'-methylenebisacrylamide in addition to rendering the photoresist color developable. The synthesis of a benzoylacetanilide analog was complicated by the instability of p-amino-benzaldehyde needed as an intermediate. Non-diffusing, water-soluble color couplers are effectively retained by the photoresist formed in the iron-peroxide system. Incorporation of a mixture of yellow, cyan and magenta non-diffusing color couplers in photopolymerizable coatings leads to photoresists that become black on color development. The processing of this system has been simplified by (1) incorporation of color developer in the coating and (2) combination of the peroxide and persulfate baths. The stability of the developer-containing coating is limited due to developer oxidation, and two developers reported to be more resistant to oxidation were prepared and tested without success.

An approach to a faster photopolymerization system based on photosensitized autoxidation of 1,3-dioxolanes has been initiated. Thus far coatings containing monomer rose bengal and the dioxolane substrate yield photoresists after moderate exposure and processing in a solution containing ferrous ion.

A gravimetric method was developed for the determination of the percent conversion of N,N'-methylenebisacrylamide to polymer when photoinitiated by the iron-peroxide system in thin gelatin layers. Both chemical and spectrophotometric evidence indicates the isolated polymer to be graft copolymer of polymethylenebisacrylamide to binder.

The photochemical chain reaction of mercuric chloride with potassium oxalate was found to photoinitiate polymerisation of A-5 solution in the absence of oxygen. Coating trials were negative.

## C. REPORTS, PUBLICATIONS, CONFERENCES, LECTURES

1. The following reports were issued:

    a. Monthly Report No. 1: "Investigation of the Photopolymerization Process," 14 February 1963 - 13 March 1963; Authors, E. Cerwonka and F. W. Millard.

    b. Monthly Report No. 2: "Investigation of the Photopolymerization Process," 14 March 1963 - 13 April 1963; Authors, E. Cerwonka and F. W. Millard.

2. A conference was held with Dr. Norman G. Gaylord, consultant on this contract, on 1 March 1963. Research progress was reviewed. A conference was also held at the U. S. Army Electronics Research and Development Laboratory on 17 April 1963 to review research progress. This meeting was attended by Miss M. Levy; Dr. E. Cerwonka represented the Photo and Repro Division of GAF.

## D. FACTUAL DATA

### 1. Photopolymerization with Ferric Salts in the Absence of Peroxides

### a. Ferric Salt of 3,3' Dihydroxybenzilic Acid

Starting with 3 hydroxybenzaldehyde, we synthesized 3,3' dihydroxybenzilic acid. Details of the preparation were given in Section D 1 a (2) of Final Report, November 15, 1962 - February 14, 1963. Coating tests were made during the past quarter to compare the behavior of the ferric salt of this acid with that of benzilic acid itself and of 4,4' dihydroxybenzilic acid.

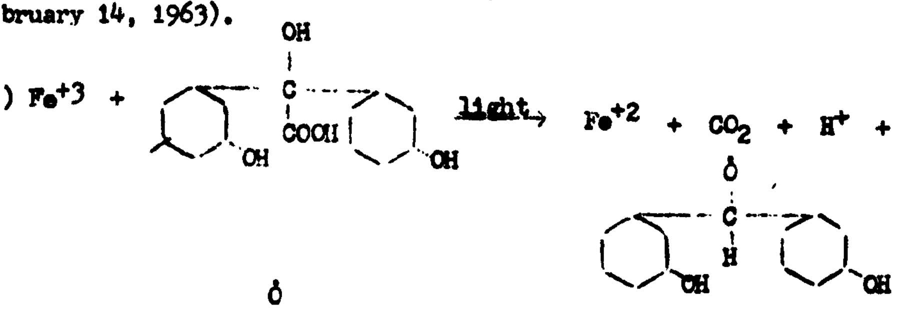
Table I

| | Recipe | | |
|---|---|---|---|
| | 0647 | 0648 | 0649 |
| Natrosol "250L" | 0.625 g. | 0.625 g. | - |
| Polyvinyl pyrrolidone, K-30 | - | - | 3.75 g. |
| MBA (N,N' methylene bisacrylamide) | 0.250 g. | 0.500 g. | 0.500 g. |
| 3,3' Dihydroxybenzilic acid (FW = 260) | 0.780 g. | 0.033 g. | 0.033 g. |
| Ferric ammonium sulfate dodecahydrate (FW = 482) | 0.723 g. | 0.060 g. | 0.060 g. |
| Water, to | 12.5 ml. | 12.5 ml. | 12.5 ml. |
| Required exposure with water wash | 60 sec. - no resist | 5 sec. - colorless resist | 5 sec. - colorless resist |
| With hydrogen peroxide wash | 5 sec. - black resist | 5 sec. - gray resist | 5 sec. - gray resist |

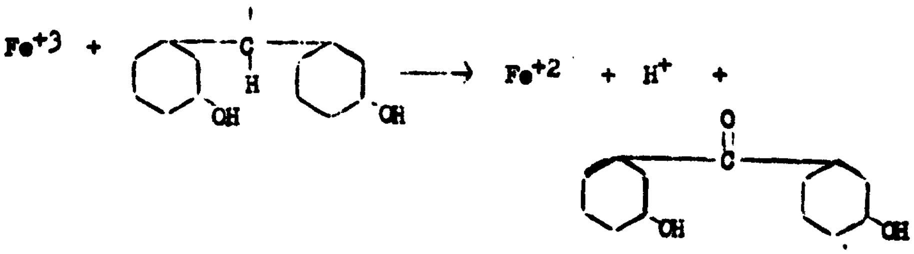
Test Procedure: 3,3' Dihydroxybenzilic acid in the quantity indicated was dissolved in deionized water (20 ml.). Binder was then stirred in, and monomer in 20 ml. water was added, the mixture being warmed at 40° C. until solution was complete. Ferric ammonium sulfate dissolved in 5 ml. water was added in red light. The solution was brought to a volume of 50 ml., coated on baryta paper, and allowed to dry. A test strip was exposed (for the period indicated in the table) to the light from a 375 watt reflector lamp at 16 inches distance. Results obtained with (a) water wash at 40°-50° C. and (b) hydrogen peroxide immersion (15 seconds) are summarized in Table I.

Discussion of Table I Data: Recipes #0648 and #0649 each contained 1/8 millimole ferric ammonium sulfate and 1/8 millimole of the benzilic acid derivative in 12.5 ml. coating solution. Test strips of each gave a colorless resist with water wash, whereas a gray color appeared during immersion in hydrogen peroxide. Hydroxyl radicals derived from the reaction of ferrous ion with hydrogen peroxide enter the aromatic ring forming a catechol derivative, which forms a colored complex with ferric ions. A test strip of #0647 contained 1.5 millimoles ferric salt and 1.5 millimoles organic acid in 12.5 ml. coating solution. This sample gave no resist with water after relatively brief exposures. It is believed that the higher concentration of ferric ion present in #0647 effects the oxidation of photoproduced diphenylmethoxyl radicals by reaction (2) below. This reaction competes with the initiation of MBA polymerization by the diphenylmethoxyl radical. Similar results were reported with ferric benzilate and other derivatives (Tables I and II, Section D, Final Report, November 15, 1962 - February 14, 1963).

(1)



(2)



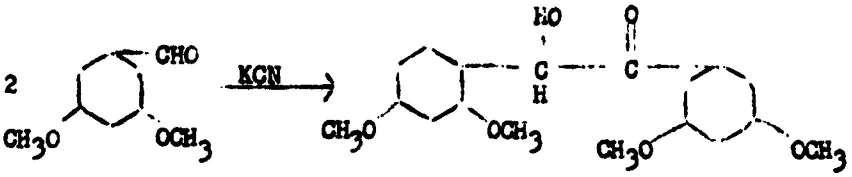
### b. Attempted Preparation of 3,5,3',5' Tetrahydroxybenzilic Acid

Results described in this and previous reports involving the ferric salt of various hydroxybenzilic acids suggest that the ferric salt of 3,5, 3',5' tetrahydroxybenzilic acid would (a) initiate polymerization of a vinyl monomer in light, (b) show greater image density when immersed in hydrogen peroxide than benzilic acids having only one hydroxy group per aromatic ring, (c) might show a greater density in the dry coated layer when exposure is followed by heating or storage in the dark (Patent Disclosure AD 1804, also earlier reports). Accordingly, the synthesis of this acid (not reported in the literature) has been undertaken.

## 3,5,3',5' Tetramethoxybenzoin

This procedure was based on a method of preparing 3,3' dimethoxybenzoin from 3 methoxybenzaldehyde(1).

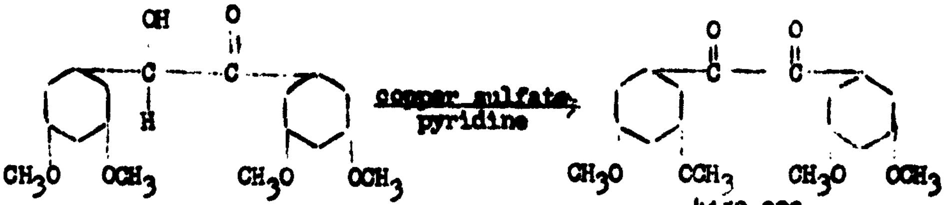
Powdered potassium cyanide (1 g.) was added to a boiling solution of 3,5 dimethoxybenzaldehyde (10 g.) in 50% aqueous ethanol (30 g.). After boiling under reflux two hours, the mixture was cooled and placed under refrigeration overnight. About 7.6 g. of an orange-yellow oil was obtained. This material was not further purified but was oxidized to a benzil derivative by a published method(2).



m.p. 85°- 88° C.

## 3,5,3',5' Tetramethoxybenzil

The oil obtained from the benzoin condensation was assumed to be 3,5,3',5' tetramethoxybenzoin formed in about 20% yield(1). It was dissolved in pyridine (5 ml.); copper sulfate (3.35 g.) in water (1.75 ml.) was added and the mixture heated under reflux two hours. At the end of this period the mixture was cooled and poured into three volumes of water, liberating a dark yellow solid. The crude material was recrystallized from 95% ethanol (30 ml.). The yield of purified 3,5,3',5' tetramethoxybenzil was 2.3 grams (11.6%) melting at 165°-166° C. The compound not having been previously prepared, a sample was submitted for analysis.

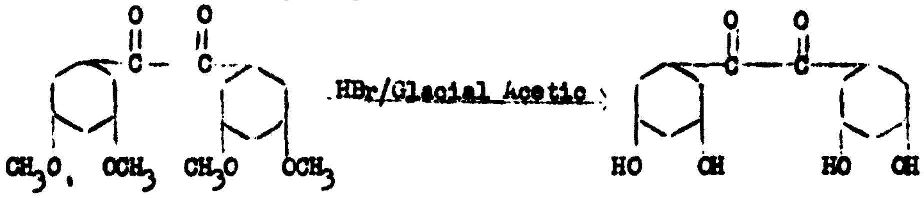


4153-239

Analytical Date: C: Calc. 65.43, Found 65.33
H: Calc. 5.50, Found 5.55

### 3,5,3',5' Tetrahydroxybenzil

Tetramethoxybenzil was converted to the tetrahydroxy compound in a manner described in the literature(2). The methoxy compound (2.3 g.) was dissolved in glacial acetic acid (20 ml.); 48% hydrobromic acid (40 ml.) was added, and the mixture heated under reflux for six hours. At the end of this period the reaction mixture was cooled and poured into water. The crude material (1.1 g.) was nearly black in color and had a melting point above 300° C. Although no single recrystallizing solvent was found, it dissolved in ethanol, from which it was re-precipitated with water.



### Attempted Synthesis of 3,5,3',5' Tetrahydroxybenzilic Acid

Following a published method(3) which had previously been found satisfactory, we attempted the conversion of tetrahydroxybenzil to tetrahydroxybenzilic acid.

3,5,3',5' Tetrahydroxybenzil (1.0 g.) was added to a melt at 125° C. consisting of sodium hydroxide (1.0 g.), potassium hydroxide (1.0 g.) and water (0.8 ml.). The mixture was stirred at 150° C. for 15 minutes (Wood's metal bath). It was then cooled, diluted with water and acidified with hydrochloric acid (10 ml. of 6N). Ether extraction (three times, 100 ml. each time) gave a trace of oily residue. Qualitative tests (ferric ammonium sulfate should give a yellow green; ferrous sulfate-hydrogen peroxide should give a black) showed that the desired product was absent in the residue and in the aqueous phase. About 0.6 g. starting material (tetrahydroxybenzil) was recovered unchanged. More drastic reaction conditions are evidently required to effect the benzilic acid transformation of this particular benzil.

### c. Other Properties of Ferric Benzilate Photocatalyst

#### (1) Thermal Fixation of Ferric Benzilate Coatings

If ferric benzilate in a coated layer can be thermally decarboxylated following exposure, the photosensitivity of the ferric salt will have been destroyed. In this way a coating having a ferric salt as photocatalyst can be thermally "fixed." Thermal fixation tests were carred out with strips of #0650, formulated as follows:

| | | |
|---|---|---|
| Polyvinyl pyrrolidone | 15 | g. |
| MBA | 2 | g. |
| Benzilic acid (recrystallized from water) (FW = 228) | 0.114 | g. |
| Ferric ammonium sulfate dodecahydrate | 0.241 | g. |
| Water, to | 50 | ml. |

Experimental: This formulation was coated in the same manner as those described in Table I. A control test strip was exposed 30 seconds to the usual light source (375 watt reflector lamp at 16 inches) followed by washout and showed a colorless resist. Another test strip was also exposed 30 seconds, heated 60 seconds in an oven at 180° C., then washed with hot water (50°-60° C.). The resist image was now largely obscured by background polymer. When an exposed (30 seconds) strip was heated 30 seconds in a 180° oven, then washed out, the background polymer had less thickness than resulted from the 60 second heating. The same exposure (30 seconds) and heating (30 seconds) were repeated, but a second exposure of 30 seconds was made at right angles to the original exposure after the intervening heating period. Washout showed only one resist image. In an effort to reduce the heating period, another sample was exposed 30 seconds, heated 10 seconds at 180° C., then re-exposed at right angles to the first exposure. Washout showed a pronounced resist image from the original exposure, with a second, less-pronounced image appearing at right angles to the first.

Discussion: In these tests a 60 second heating period was excessive and effected polymerization or hardening of the background. The hardened layer could not readily be washed out. Insufficient heating was illustrated by the 10 second period, which permitted the photocatalyst to retain its sensitivity to light and gave a double image after washout. The degree of thermal fixation, therefore, depends on an optimum heating period at a particular temperature.

### (2) Sensitizing of Ferric Benzilate to Red Light

To determine whether the addition of methylene blue to a photopolymerizable ferric benzilate composition makes the coated layer red light sensitive, we prepared and coated the following formulations:

Table II

| | 0692 | 0693 | 0694 |
|---|---|---|---|
| Natrosol, "250L" | 1.25 g. | 1.25 g. | 1.25 g. |
| MBA | 1.0 g. | 1.0 g. | 1.0 g. |
| Benzilic acid (recrystallized from water) FW=228 | 0.057 g. | 0.057 g. | 0.057 g. |
| Methylene Blue, aq. (374 mg. per 100 ml.) FW = 374 | 5 ml. | - | 5 ml. |
| Ferric ammonium sulfate dodecahydrate (FW=482) | 0.120 g. | 0.120 g. | - |
| Water, to | 25 ml. | 25 ml. | 25 ml. |

Test strips wereexposed through a negative to a 375 watt lamp at 16 inches for a period of three minutes. A Hersol red filter was placed in series with the negative. Washout showed resist images present on samples of #0692 and #0694. #0693 showed no trace of image. The compositions containing methylene blue are indeed sensitive to red light, but it is not clear from our test data whether the initiating species is a diphenylmethoxyl radical derived from ferric benzilate (#0692) or a radical arising from photo-excited methylene blue--with benzilic acid acting as electron donor (#0694).

(3) Reduction of Silver Nitrate by Exposed Ferric Benzilate

Print-out systems based on the reduction of silver ion to metallic silver by photoformed ferrous ion have been known for many years. The action of light photoreduces ferric benzilate with the simultaneous formation of an initiating radical and a ferrous ion. A coated layer containing monomer and silver nitrate would be expected to show polymer and metallic silver in exposed areas.

Table III

| | 0745 | 0747 | 0750 |
|---|---|---|---|
| PVP | 7.5 g. | 7.5 g. | 7.5 g. |
| MBA | - | 1.0 g. | 1.0 g. |
| Silver nitrate (FW=170) | 0.170 g. | 0.340 g. | 0.170 g. |
| Benzilic acid (FW= 228), EK White Label | 0.057 g. | 0.057 g. | - |
| Oxalic acid, anhydrous (FW=90) | - | - | 0.045 g. |
| Ferric ammonium sulfate dodecahydrate (FW=482) | 0.120 g. | 0.120 g. | 0.120 g. |
| Water, to | 25 ml. | 25 ml. | 25 ml. |

The formulations were prepared and coated on baryta paper in red light. Samples were exposed five seconds to the usual light source. No image was visible immediately after exposure; however, wetting produced a brown image in samples #0745 and #0747. (The presence of water accelerates the reduction of silver ion by ferrous.) Further washing with hot water left a relief image on #0747, brown in color. #0745 showed brown color in the exposed areas of the paper, but no resist (print-out silver only). #0750 showed nothing at five seconds, but a relief image of a gray color was obtained after exposure for 30 seconds followed by washout (reduction of silver by ferrous oxalate--initiation of polymerization by oxalate with relatively long exposure). When the exposed sample of #0747 was washed in

1% hydrogen peroxide, a colorless resist was obtained. This may be attributed to reoxidation of metallic silver by peroxide or to reoxidation of ferrous to ferric by peroxide so that the silver nitrate was not reduced.

## 2. Photopolymerization Initiated by Uranyl and Ceric Salts

### a. Aqueous Solutions of Uranyl Salts

Studies of the rate of oxidation of mandelic acid by methylene blue in the presence of uranyl nitrate, $UO_2(NO_3)_2$, as photosensitiser have been made by Ghosh, Narayanmurti and Roy(4). These authors postulate the photoreduction of uranyl ($UO_2^{+2}$) to uranous ($UO^{+2}$) ion, accompanied by the oxidation of mandelic acid to benzaldehyde. Methylene blue serves to reoxidise the reduced ion $UO^{+2}$ to $UO_2^{+2}$, concurrent with the reduction of the dye to its leuco form. The ion $UO_2^{+2}$ now becomes available for photoreduction again. The sequence of reactions is depicted by the following equations:

(1) $UO_2^{+2} + C_6H_5CHOH\ COOH \xrightarrow{light} UO^{+2} + C_6H_5CHO + CO_2 + H_2O$

(2) $UO^{+2}$ + methylene blue $\longrightarrow$ $UO_2^{+2}$ + leuco methylene blue

(3) Leuco methylene blue + $O_2 \longrightarrow$ methylene blue + 2 •OH

Reaction (3) is suggested by Oster as functioning during the initiation of polymerization by photoreducible dyes(5). Reactions (2) and (3) indicate the regeneration of uranyl ($UO_2^{+2}$)ion and methylene blue during the cycle.

The fact that there are three wavelengths to which uranyl ion is sensitive (reaction (1) ), coupled with the possibility that reaction (1) may proceed at a high velocity impelled us to begin an investigation of this cyclic reaction, attempting to apply it to the polymerisation of vinyl monomers.

A number of experiments were carried out in aqueous solutions. The results are summarised in Table IV.

Table IV

| | Induction Period Minutes : Seconds |
|---|---|
| Uranyl nitrate (FW=502), 0.502 g. | 0:40 |
| Uranyl nitrate, 0.502 g.<br>Mandelic acid, 0.152 g. (F.W=152) | 0:53 |
| Uranyl nitrate, 0.502 g.<br>Methylene blue (FW=374) $3.74 \times 10^{-6}$ g.<br>(~$10^{-5}$ millimole) | 0:43 |

Table IV (continued)

| | Induction Period Minutes : Seconds |
|---|---|
| Uranyl nitrate, 0.502 g.<br>Mandelic acid, 0.152 g.<br>Methylene blue, $3.74\times10^{-6}$ g. | 0:59 |
| Uranyl nitrate, 0.200 g. (0.2 millimole) | 0:48 |
| Uranyl Nitrate, 0.201 g.<br>Mandelic Acid, 0.031 g. (0.2mm) | 1:03 |
| Uranyl nitrate, 0.201 g.<br>Methylene blue, $3.74\times10^{-6}$ g. | 0:54 |
| Uranyl nitrate, 0.201 g.<br>Mandelic acid, 0.031 g.<br>Methylene blue, $3.74\times10^{-6}$ g. | 1:07 |

**Experimental:** To 5.0 ml. A-5, magnetically stirred in red light in a 20 ml. beaker, there was added the quantities of material listed above, dissolved in a total of 1.0 ml. of water. (Total volume = 6.0 ml. in each experiment.) Each solution was irradiated with a 1000 watt tungsten lamp at 23 cm. When the gel point was reached as shown by an abrupt cessation of stirring, the time to gelation was recorded as "Induction Period."

**Discussion of Table IV Data:** The induction period was shorter with higher uranyl nitrate concentration. Addition of mandelic acid, methylene blue, or a combination of both lengthened the induction period over the range of concentration at uranyl ion studied. Whether the addition of methylene blue has sensitized the solution to red light has not been determined.

An unknown factor in these reactions is the nature of the radical which initiates polymerization when only uranyl nitrate is present. The induction period is shortest in this instance (0:40). From our data it appears that the oxidation of mandelic acid by uranyl nitrate competes with chain initiation and propagation effected by the uranyl salt. To gain more insight into the mechanism of photopolymerization sensitized by uranyl salts, we have studied the photopolymerization of uranyl acrylate. When a solution of uranyl acrylate is exposed to visible light, a white opaque polymer forms. Evidently the acrylate anion is oxidized to a free radical species which initiates the polymerization of other acrylyl radicals or acrylate anions.

Uranyl acrylate as employed in our tests was derived in either of two ways: (a) uranium trioxide was dissolved in acrylic acid, or (b) uranyl nitrate was neutralized with sodium acrylate. Table V lists examples of the tests.

## Table V

| | Solution | | Volume of Sample | Induction Period (Minutes: Seconds) |
|---|---|---|---|---|
| (a) | Uranium trioxide (FW=286) | 0.572 g. | | |
| | Acrylic acid (vacuum distilled, contains no inhibitor)(FW=72) | 0.4 g. | | |
| | Water | 10 ml. | 1.0 ml. | 0:15 |
| | Concentration: 2mmoles $UO_2^{+2}$ per 10 ml. water over 4mmoles acrylic acid per 10 ml. water | | | |
| (b) | Uranium trioxide | 0.572 g. | | |
| | Acrylic acid, (commercial grade, contains p-methoxyphenol as inhibitor) | 0.4 g. | | |
| | Water | 10 ml. | 1.0 ml. | 0:16 |
| (c) | Solution (a) | | 0.5 ml. | |
| | Water | | 0.5 ml. | 0:27 |
| (d) | Solution (b) | | 0.5 ml. | |
| | Water | | 0.5 ml. | 0:26 |
| (e) | Solution (a) | | 0.2 ml. | |
| | Water | | 0.8 ml. | 0:57 |
| | (Polymer formed first at rear of test tube) | | | |
| (f) | Uranium trioxide | 0.143 g. | | |
| | $(CH_2{=}CHCONH)_2CHCOOH$ (FW=198) | 0.198 g. | | |
| | Water | 5 ml. | 1.0 ml. | 1:05 |
| (g) | Solution (b) | | 0.5 ml. | |
| | Solution (f) | | 0.5 ml. | 0:24 |
| (h) | Uranyl nitrate (FW=502) | 1.004 g. | | |
| | Solution of sodium acrylate | 10 ml. | 1.0 ml. | 0:17 |
| | (Solution contains 0.720 gram acrylic acid, commercial grade, neutralized with 0.620 gram sodium carbonate monohydrate in a total of 25 ml. aqueous solution) | | | |
| | Concentration: 2 mmoles $UO_2^{+2}$ )<br>4 mmoles acrylate) 10 ml. solution | | | |

Table V (continued)

| Solution | | Volume of Sample | Induction Period (Minutes: Seconds) |
|---|---|---|---|
| (i) Uranyl nitrate | 0.200 g. | | |
| Solution of sodium acrylate [same as in (h)] | 2 ml. | | |
| Water | 8 ml. | 1.0 ml. | 1:14 |
| (j) Solution (b) | | 1.0 ml. | |
| Methylene blue (FW=374) 3.74 mg. per 100 ml. aq. solution | | 0.1 ml. | 0:18 |
| Concentration: Methylene blue: $10^{-5}$ mmole/0.1ml. | | | |
| (k) Solution (a) | | 1.0 ml | |
| Methylene blue, 30 mg. per 100 ml. aq. | | 0.1 ml. | 0:18 |
| Concentration methylene blue: $8x10^{-5}$ mmole/0.1 ml. | | | |
| (l) Solution (k) | | 1.1 ml. | |
| Versene solution, $8x10^{-5}$ mmole/0.1 ml. (contains 30 mg. disodium versene (FW=372) dissolved in 100 ml. aqueous solution) | | 0.1 ml. | 0:20 |
| (m) Solution (b) | | 0.5 ml. | |
| Acrylic acid solution (7.2 g. commercial acrylic acid in 50 ml. aq. solution) | | 0.5 ml. | 0:28 |
| Ratio excess acrylic acid:uranyl ion = 10:1 | | | |
| (n) Solution (h) | | 0.5 ml. | |
| Sodium acrylate solution (7.2 g. acrylic acid, commercial grade, neutralized with sodium carbonate monohydrate, 6.2 g., in a total volume of 50 ml. aq. solution) | | 0.5 ml. | 0:27 |
| Ratio of excess acrylate ion:uranyl ion = 10:1 | | | |
| (o) Uranyl methacrylate solution | | 1.0 ml. | 0:16 |
| (Sodium methacrylate (FW=108) | 0.432 g. | | |
| Uranyl nitrate (FW=502) | 1.004 g. | | |
| to 10.0 ml. with water) | | | |
| (p) Uranyl methacrylate solution (solution contains $UO_3$*, 0.572 g., and methacrylic acid (FW=86), 0.344 g. | | 1.0 ml. | 2:00 |

*$UO_3$ only partially dissolved after three weeks

Experimental: Volume indicated for each sample was pipetted (in red light) into a test tube (inside diameter = 1 cm., depth = 7.5 cm.) which was placed at a distance of 23 cm. from the outer surface of a 1000 watt tungsten lamp. A glass, water-filled cell, one cm. inside thickness, was interposed between the lamp and the test tube to absorb heat. When the lamp was turned on, the induction period was measured by means of a stop watch. The time taken was that elapsing until polymer began to form. The first appearance of white opaque polymer showed at the edge of the solution nearer the lamp. In experiment (e) as noted above the polymer layer formed first at the edge of the solution farther from the lamp. The opaque white character of this polymer resembled that arising from MBA monomer, rather than the transparent product from A-5.

Discussion of Data from Table V: There was no significant difference between the induction periods of samples photocatalyzed by uranyl acrylate from $UO_3$-acrylic acid as compared with those photocatalysed by uranyl acrylate from uranyl nitrate and sodium acrylate. Moreover, no difference was observed in the behavior of acrylate derived from distilled acrylic acid (inhibitor-free) and commercial acrylic acid (containing p-methoxyphenol as inhibitor). The shortest induction periods were observed when uranyl concentration was highest. A carboxylic acid derived from acrylamide (f) was less soluble than acrylic acid and dissolved less uranium trioxide. The presence of methylene blue (k), (l) had no appreciable effect on the induction period. Excess acrylic acid or acrylate ion (m), (n) did not materially affect the induction period—compare (d). Samples of solutions (a), (b), (f) and (h) have not polymerized in the absence of light during a two-month test period. Methacrylic acid dissolved uranium trioxide at a slower rate than acrylic acid.

b. Coated Layers of Uranyl Salts

To take advantage of some of the relatively short induction periods listed in Table V we require a carrier or binder that is compatible with uranyl salts. A hardening reaction takes place between uranium nitrate and PVP (#0688). The test recipe consisted of PVP, 3.75 g., and uranyl nitrate, 0.502 g., brought to 12.5 ml. with water. A remix of this formulation which included MBA, 0.5 g., became hardened in the same manner when the uranium salt was added. Neither formulation could be coated. Combination of uranyl nitrate with each of several organic acids also hardened or thickened PVP. In recipe #0713, formic acid (FW=46), 0.051 g. was added to 0.502 g. uranyl nitrate, 0.5 g. MBA and 3.75 g. PVP in 12.5 ml. solution. Lactic acid (FW=80), 85% aq., 0.1 ml. was added to the same quantities of uranyl nitrate, MBA and PVP, to give #0719. Mandelic acid (FW=152), 0.304 g. in recipe #0705, also a double quantity, 0.608 g., in recipe #0706, were added separately to uranyl nitrate 0.502 g., MBA, 0.500 g., and PVP, 3.75 g., the solution being brought to 12.5 ml. with water. In recipe #0738, acrylic acid (FW=72), 0.144 g. was added to uranyl nitrate, MBA and PVP. All these solutions became hardened almost at once when the ingredients were mixed. There was no hardening observed when pure uranyl formate, 0.360 g., was added to MBA, 0.500 g., and PVP, 3.75 g., in 12.5 ml. solution. Likewise uranyl acetate, 0.424 g., added to PVP, 3.75 g., in 12.5 ml. solution produced no hardening. In a number of other tests uranyl nitrate was mixed with the stoichiometric equivalent of the sodium salts of organic acids as listed in Table VI.

Table VI

| Recipe | Salt | Formula Weight | Formula Used |
|---|---|---|---|
| #0715 | Sodium formate | 68 | 0.136 g. |
| #0696 | Sodium acetate trihydrate | 136 | 0.272 g. |
| #0720 | Sodium lactate | (Solution prepared from sodium carbonate monohydrate, 0.124 g., and lactic acid, 85% aq., 0.19 ml.) | |
| #0716 | Sodium mandelate | (Solution prepared from sodium carbonate monohydrate, 0.124 g., and mandelic acid (FW=152), 0.304 g.) | |

These combinations of uranyl nitrate, 0.502 g., and the respective sodium salt did not harden the PVP colloid (3.75 g.) in the presence of MBA, 0.500 g., made up to 12.5 ml. solution with water.

The effect of pH alone on PVP was checked. A 10% aqueous solution of uranyl nitrate showed a pH of 2.1. To a PVP solution (3.75 g. in 12.5 ml. solution) without added uranium salt there was added 6N nitric acid (0.33 ml.), which lowered the pH to 1.5. There was no hardening action. It is the cross-linked uranyl-polyvinylpyrrolidone complex which appears to be pH sensitive.

A number of uranyl salt-MBA coatings were prepared using PVP as binder. In all cases, long exposures (three minutes or more) were required to produce a resist after water wash. Two of the tested formulations are listed.

Table VII

| | #0698 | #0731 |
|---|---|---|
| Polyvinylpyrrolidone, K-30, Antara | 3.75 g. | 3.75 g. |
| MBA | 0.5 g. | 0.5 g. |
| Uranyl acetate (FW=424) | 0.424 g. | - |
| Uranyl nitrate (FW=502) | - | 0.502 g. |
| Sodium acrylate, aq.* | - | 5.0 ml. |
| Water, to | 12.5 ml. | 12.5 ml. |

* Solution consists of acrylic acid, commercial grade, 0.720 g. and sodium carbonate monohydrate, 0.620 g., dissolved in 25 ml. aqueous solution.

The formulations were coated on baryta paper and allowed to dry in red light. Samples were exposed through a negative for five minutes to the light from a 375 watt tungsten lamp at 16 inches. Washout showed a faint image in each case.

Hydroxyethyl cellulose (Natrosol) was not hardened by uranyl nitrate. It served as a carrier by means of which the accelerating action of a few organic compounds was tested. The more effective recipes are listed in Table VIII.

Table VIII

| | #0687 | #0724 | #0725 |
|---|---|---|---|
| Natrosol, 250L | 0.625 g. | 0.625 g. | 0.625 g. |
| MBA | 0.500 g. | 0.500 g. | 0.500 g. |
| Uranyl nitrate (F#=502) | 0.502 g. | 0.502 g. | 0.502 g. |
| Formic Acid, 90% | - | 0.05 ml. | - |
| Dextrose, anhydrous | - | - | 0.540 g. |
| Uranyl acrylate* | - | - | - |
| Sodium acrylate, aq. | - | - | - |
| Water, to | 12.5 ml. | 12.5 ml. | 12.5 ml. |
| Exposure required: | 30 seconds | 30 seconds | 15 seconds |

| | #0734 | #0753 | #0755 |
|---|---|---|---|
| Natrosol, 250L | 0.625 g. | 0.625 g. | 0.625 g. |
| MBA | - | 0.500 g. | 0.500 g. |
| Uranyl nitrate (F#=502) | 0.502 g. | - | 0.502 g. |
| Formic acid, 90% | - | - | - |
| Dextrose, anhydrous | - | - | - |
| Uranyl acrylate* | - | 0.412 g. | - |
| Sodium acrylate, aq. | 5.0 ml.*** | - | 2.5 ml.** |
| Water, to | 12.5 ml. | 12.5 ml. | 12.5 ml. |
| Exposure required: | 3 minutes | 15 seconds | 30 seconds |

*From $UO_3$, 1.144 g. and acrylic acid, 0.8 ml., in 5 ml. water. The undissolved uranyl acrylate was filtered in red light and dried.

**Contains acrylic acid (commercial grade), 1.44 g., and sodium carbonate monohydrate, 1.24 g., in 25 ml. aqueous solution.

***Acrylic acid (commercial grade), 0.720 g., and sodium carbonate monohydrate, 0.620 g., in 25 ml. aqueous solution.

The formulations were coated and tested in the same manner as those described in Table VII. The minimum exposures as tabulated indicate some accelerating action by dextrose (#0725). Pure uranyl acrylate also forms an effective recipe (#0753).

c. <u>Ceric Salts, Solutions and Coatings</u>

Ceric acrylate solution behaves in some respects like uranyl acrylate when exposed to light. A solution was prepared in red light as follows:

| | | |
|---|---|---|
| Ceric ammonium nitrate (FW=548) | 1.096 | g. |
| Acrylic acid (FW=72) (EK White Label) | 0.576 | g. |
| Water, to | 10 | ml. |

Exposure of 1.0 ml. of solution to a 1000 watt tungsten lamp at 23 cm. produced an opaque polymer in one minute five seconds.

A control solution consisted of

| | | |
|---|---|---|
| Ceric ammonium nitrate | 1.096 | g. |
| MBA, 4 g. per 100 ml. aq. | 10 | ml. |

Exposure of 1.0 ml. of the control solution for a period of ten minutes (same light source) showed no reaction.

The stored ceric acrylate solution described above showed the deposit of a white precipitate after several hours. The nature of this material is not known. Dilute nitric acid dissolved some of the material with the formation of a yellow solution. This suggests that ceric oxide, $CeO_2$, forms part of the deposit. Polymer was absent so far as could be determined.

Another test solution contained

| | | |
|---|---|---|
| Ceric ammonium nitrate | 1.096 | g. |
| Methacrylic acid (FW=86) | 0.688 | g. |
| Water, to | 10 | ml. |

This solution produced a voluminous white precipitate while stored in red light for a few minutes. Oxidation of the organic compound is probably taking place.

Ceric oxide, $CeO_2$, did not dissolve in acrylic acid. Ceric acrylate as a consequence could not be prepared from the oxide as was uranyl acrylate from $UO_3$.

Addition of a solution of ceric ammonium nitrate to a solution of sodium acrylate caused precipitation of ceric oxide at this pH.

It was found possible to prepare a coating of ceric acrylate as follows:

**Recipe #0757**

| | | |
|---|---|---|
| PVP | 3.75 | g. |
| MBA | 0.5 | g. |
| Acrylic acid (FW=72) (EK White Label) | 1.44 | ml. |
| Ceric ammonium nitrate (FW=548) | 0.548 | g. |
| Water, to | 12.5 | ml. |

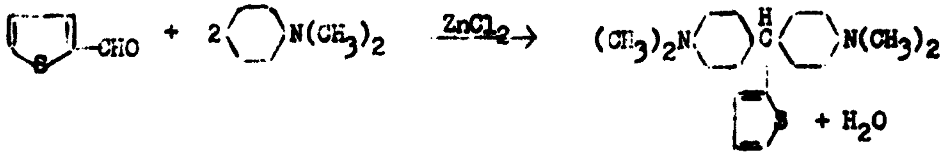
The solution was coated in red light on baryta paper and allowed to dry. Exposure of a sample through a negative for five seconds to the usual light source, followed by washout, showed a resist image. The coating has been stable in the dark for over six weeks.

## 3. Formation of Colored Images in Order to Eliminate Incorporation of Dyes in Coatings

### a. Colored Images Resulting from Dye-Radical Interaction

As a continuation of the work described in Section D.2.a. of Final Report, November 15, 1962 - February 14, 1963, we prepared the leuco base of "thiophene green" (also called "thiophene malachite green")(6). The objective of this research was the formation of a colored image during exposure of a light-sensitive ferric salt.

Zinc chloride (10 g.) was fused in a porcelain evaporating dish, cooled and powdered. It was then added to a mixture of 25 g. dimethylaniline and 10 g. thiophene-2-aldehyde. The mixture was heated on the steam bath with frequent stirring for four hours. Water was then added, liquefying the viscous mass, and the hot liquid was poured into a 500 ml. round-bottom three-necked flask. Steam distillation was carried out until droplets of oil no longer came over. The suspension in the flask was cooled and the water removed by decantation as much as possible. The solid was now dissolved in hot ethanol and the solution filtered hot, removing a green residue. The alcoholic solution was kept under refrigeration overnight. The product was a gray-green solid. Seven grams were obtained from the first crystallisation and an additional gram from the mother liquor after it had stood another day. A sample recrystallized from hexane melted at 94°-95° C. (lit. 92°-93° C.)(6).



Samples of this leuco base were tested in coated layers as follows:

Table IX

| | #0674 | #0677 | #0678 | #0679 | #0680 |
|---|---|---|---|---|---|
| Polyvinylpyrrolidone K-30 | 7.5 g. | 7.5 g. | 7.5 g. | 7.5 g. | 7.5 g. |
| Benzilic acid, recrystallized | - | 0.228 g. | - | - | 0.228 g. |
| Oxalic acid | - | - | 0.090 g. | - | - |
| Leuco base of thiophene malachite green (FW=215) | 0.054 g. | 0.054 g. | 0.054 g. | 0.054 g. | 0.054 g. |
| Hydrochloric acid, 1N | 0.50 ml. | 0.50 ml. | 0.50 ml. | 0.50 ml. | 0.50 ml. |
| Ferric ammonium sulfate dodecahydrate | - | 0.015 g. | 0.015 g. | 0.030 g. | 0.030 g. |
| Water, to | 25 ml. | 25 ml. | 25 ml. | 25 ml. | 25 ml. |
| Color, unexposed coating | White | Faint green tint | Light green | Dark green | Faint green tint |
| Three-minute exposure | No image | Green print-out | Green print-out | No image visible | Green print-out |

(Recipes coated and tested in the same manner as those in Table VIII.)

Discussion of Table IX Data: The resistance to air and light of leuco thiophene green hydrochloride has been noted by Armstrong and Grant(7). Ferric ion not complexed with an organic acid oxidized the leuco dye to its colored form in the dark (#0679). Ferric ion in combination with excess oxalic acid (1:32 molar ratio) effected a gradual oxidation of the leuco dye in the dark as the coating aged (#0678). The benzilate coatings (#0677 and #0680) required approximately the same exposure, although the iron concentrations varied. The color of the unexposed coating was not white as in the case of #0674. However, there was no perceptible increase in color density of the unexposed coating during a ten-day period. The fact that the leuco thiophene green in combination with ferric benzilate does not become oxidized to the colored form in the absence of light is an encouraging feature of the system. The rate of print-out in light is comparatively slow.

### b. Photoformation of Peroxide with Leuco Crystal Violet

These tests represent a continuation of work described in Section D.2.a. of Final Report, November 15, 1962 - February 14, 1963. The object was to determine whether a per compound was formed in appreciable concentration when certain leuco dyes are oxidized by light. The formation of a per compound in proportion to light exposure would in the presence of ferrous ion and monomer produce a polymeric image during irradiation.

The photo-oxidation of certain leuco dyes (e.g., leuco crystal violet hydrochloride) to the colored dye form is known to take place in the absence of other photocatalysts (such as ferric salt). Gros(8) believed that peroxides were formed in traces when the leuco dye was photo-oxidized.

Table X

| | #0669 | | #0684 | | #0690 | | #0704 | |
|---|---|---|---|---|---|---|---|---|
| Polyvinylpyrrolidone | 3.75 | g. | 3.75 | g. | 3.75 | g. | 3.75 | g. |
| MBA | - | | 0.5 | g. | 0.5 | g. | 0.5 | g. |
| Leuco base of crystal violet* recrystallized from hexane | 0.047 | g. | 0.047 | g. | 0.047 | g. | 0.047 | g. |
| Hydrochloric acid, 1N | 0.38 | ml. | 0.38 | ml. | 0.38 | ml. | 0.38 | ml. |
| Ferrous ammonium sulfate (FW=392) | - | | - | | 0.049 | g. | 0.025 | g. |
| Water, to | 12.5 | ml. | 12.5 | ml. | 12.5 | ml. | 12.5 | ml. |

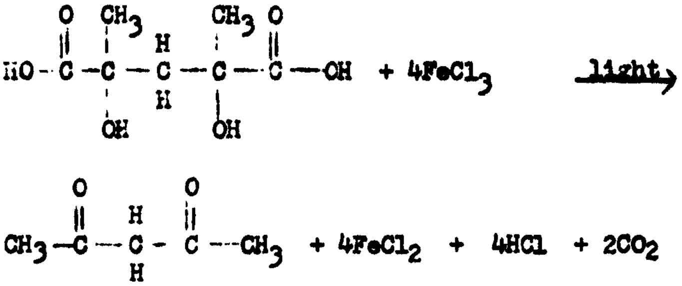
*FW=374

Solutions were coated in red light and allowed to dry. Samples of all four recipes were exposed to the light from a 375 watt reflector lamp at 16 inches for a period of three minutes. Blue print-out was evident in all cases. Washout with water (40-50° C.) showed a resist image in two samples (#0690, #0704). The other washed samples showed dye in the exposed areas but no relief image.

The results are interpreted as indicative of some polymer formation during exposure of the samples containing ferrous ion. The nature of the photoformed per compound is not known.

### c. Photoformation of Ferric Acetylacetonate

The chelate ferric acetylacetonate has a red color. We have earlier proposed that acetylacetone be photoformed in a coated layer. This could in theory be effected by the photodecomposition of the ferric salt of 1,3 dihydroxy 1,3 dimethylglutaric acid.

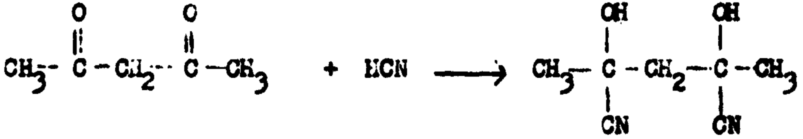


$$HO-\overset{\overset{O}{\parallel}}{C}-\underset{\underset{OH}{|}}{\overset{CH_3}{\overset{|}{C}}}-\underset{H}{\overset{H}{C}}-\underset{\underset{OH}{|}}{\overset{CH_3}{\overset{|}{C}}}-\overset{\overset{O}{\parallel}}{C}-OH + 4FeCl_3 \xrightarrow{\text{light}}$$

$$CH_3-\overset{\overset{O}{\parallel}}{C}-\underset{H}{\overset{H}{C}}-\overset{\overset{O}{\parallel}}{C}-CH_3 + 4FeCl_2 + 4HCl + 2CO_2$$

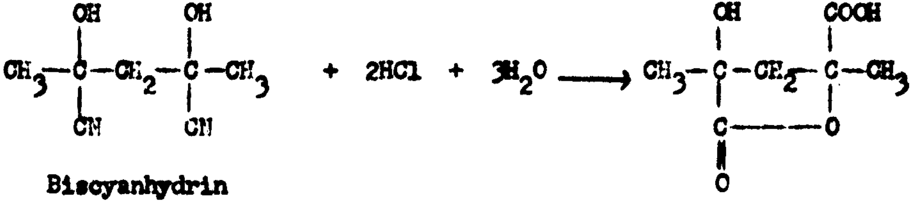
Although ferrous ion is formed which does not form a colored complex with acetylacetone, we believe that aerial oxidation of ferrous to ferric would take place within a short time after exposure.

The desired acid--1,3 dihydroxy 1,3 dimethyl glutaric acid--was synthesized by the method of Zelinsky(9). 2,4 Pentanedione, 20 g., was added dropwise with stirring to a solution of potassium cyanide, 26 g., in 20 ml. of water. The temperature was not allowed to exceed 15° C. A precipitate of potassium salt formed. This salt was redissolved by the dropwise addition of 40 ml. water, with stirring and cooling ( 15° C.). Next concentrated hydrochloric acid, 17 ml., was added with cooling ( 15° C.), thereby precipitating the biscyanhydrin. This material was filtered, washed with cold water until white, and dried on a suction funnel. Melting point was 134-136° C. It was not recrystallized. The yield is practically quantitative.



$$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3 + HCN \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

The biscyanhydrin was now converted to the "lactonic acid" as follows. Concentrated hydrochloric acid, 17 ml., was added to the dry biscyanhydrin in an evaporating dish under the hood. The solution evolved heat; it was allowed to cool and stand overnight. Later it was evaporated to dryness on the steam bath, and extracted with ether. Extraction with seven 300 ml. portions of dry ether yielded 7.2 grams lactonic acid after evaporation of the ether in vacuo. Melting point of the product was 192°-193° C. It was not recrystallized.

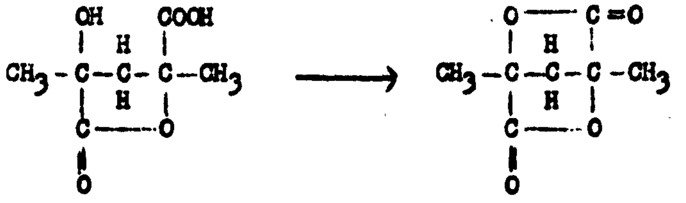


Biscyanhydrin

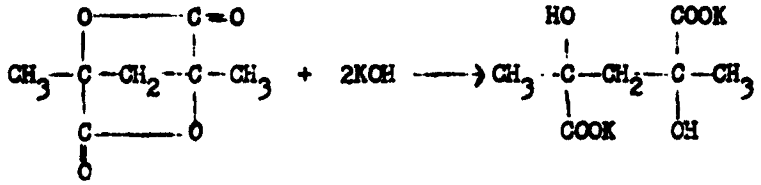
Lactonic acid

+ 2NH$_4$Cl

The lactonic acid, also termed the monolactone, was now distilled at atmospheric pressure, using a Wood's metal bath for heating. At a stillhead temperature of 235°-260° C., the dilactone collected in the condenser. The product was washed with cold water on a Buchner funnel to remove traces of a yellow oil. It had a melting point of 103°-104° C. 1.7 g. dilactone were obtained.



The dilactone (1.7 g.) was boiled three hours (reflux condenser) with potassium hydroxide solution (1.34 g. KOH in 50 ml. water). It was then cooled and neutralized with 4 ml. sulfuric acid, 6N. Extraction of the solution with one liter of ether in 100 ml. portions yielded 0.85 g. of the dihydroxyacid, m.p. 107°-110°. Zelinsky reported 103°-104° C.(9).



The acid was included in the following coatings:

| | #0812 | #0813 |
|---|---|---|
| Natrosol 250L | 0.312 g. | 0.312 g. |
| MBA | 0.125 g. | 0.125 g. |
| Ferric ammonium sulfate dodecahydrate | 0.361 g.<br>(0.75 mm) | 0.723 g.<br>(1.5 mm) |
| 1,3 Dihydroxy 1,3 dimethyl glutaric acid (FW = 192) | 0.072 g.<br>(0.375 mm) | 0.072 g. |
| Ammonium hydroxide, 1N | 0.75 ml. | 0.75 ml. |
| Water, to | 6.25 ml. | 6.25 ml. |

The solutions were coated on baryta paper in red light as usual. Test samples were exposed 10 seconds to the usual light source, immersed in hydrogen peroxide, 1%, and washed out. A resist remained in each case. Several exposed strips were stored in the dark room and in a 50° oven, but did not develop the desired color within several days.

Due to the tendency of the acid to lactonize at room temperature as reported by Zelinsky, there is a consequent loss of light sensitivity of the ferric salt. The formation of a single lactone ring means that the compound is no longer an alpha hydroxyacid. The fact that our test strips gave images with 10 seconds' exposure indicates that we had considerable free acid in the coating. In making additional coatings, we plan to increase the concentration of the acid. This should have the double effect of increasing coating speed and of producing more acetylacetone (pentanedione) after exposure.

### d. Colored Polymers from Colorless Monomers

#### N,N'-Methylenebisacrylamide Derivatives

One approach to the development of a dry processable photographic system based on photopolymerization is predicated on the formation of color as a consequence of polymerization. As outlined in the previous Quarterly Report (Section D-6), the preparation and evaluation of vinyl monomers having a color forming moiety present in the molecule was undertaken as an initial step in this general approach to dry processing. At that time, the synthesis and evaluation in the iron-peroxide photopolymerization system of several acrylamide and methacrylamide derived color former monomers were reported. These, and related examples described in the patent literature, are all obtained by acrylation or methacrylation of amino substituted color coupler nuclei of the type widely employed in conventional photography. None of the monomers was of the divinyl or cross-linking type. N,N'-Methylenebisacrylamide, a divinyl cross-linking type of monomer, has proven to be superior to acrylamide in a number of photopolymerization systems developed in the Ansco Laboratories in that its use generally leads to better shelf stability (resistance to autopolymerization) and better insolubility of the photoresist image at lower monomer concentrations. In hope of conferring these desirable properties to color former monomers, the preparation of N,N'-methylenebisacrylamide derivatives of color former molecules was attempted. The following reaction utilized in the commercial preparation of N,N'-methylenebisacrylamide from acrylamide and formaldehyde(10) was chosen as the basic reaction for the synthesis.

$$R{-}CHO + CH_2{=}CH{-}CONH_2 \xrightarrow{H^+} (CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH)_2{-}CHR$$

When R = a benzoylacetanilide, pyrazolone or phenolic nucleus oxidative coupling with a p-amino-N,N-dialkylaniline color developer leads to a yellow, magenta or cyan dye, respectively.

The synthesis of a cyan dye forming monomer in which the R of the above equation is equal to a 2-hydroxyphenyl group was accomplished by the following procedure:

N,N'-(2-Hydroxybenzylidene)-Bisacrylamide. A solution of acrylamide (28.4 g., 0.4 mole) and salicylaldehyde (24.2 g., 0.2 mole) in 60 ml. of ethylene dichloride containing 2 ml. of concentrated hydrochloric acid was stirred at ambient temperature under nitrogen for 13 hours. The reaction mixture was then refluxed for one hour, chilled in an ice bath and filtered. The crude product was then washed successively with water and ether to remove unreacted starting material and recrystallised from methanol. Five grams (10%) of a colorless solid, m.p. 217°, were obtained.

Analysis: Calculated for $C_{13}H_{19}N_2O_3$: C, 63.40; H, 5.73; N, 11.37.
Found: C, 63.13, 63.25; H, 5.54, 5.72; N, 11.66, 11.27.

Infrared analysis was also consistent with the proposed structure.

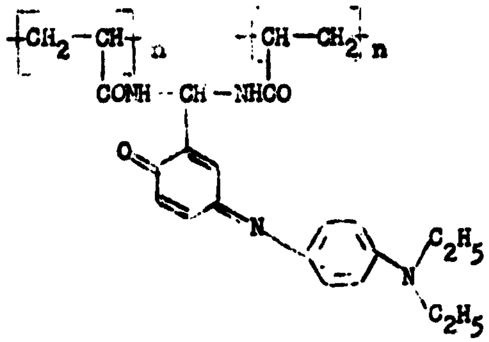
The following formulations were coated on paper base for trial of the new color former monomer in the iron-peroxide photopolymerization system.

| | 4155-177-A | 4155-177-B |
|---|---|---|
| Gelatin, Atl. 10299, 10% | 30 ml. | 30 ml. |
| Ethanol, 95% | 30 ml. | 30 ml. |
| Ferric ammonium citrate, brown, 36% | 2 ml. | 2 ml. |
| N,N'-(o-Hydroxybenzylidene)-bisacrylamide | 0.50 g.<br>(2 mmole) | - |
| N,N'-Methylenebisacrylamide | - | 0.31 g.<br>(2 mmole) |
| Saponine, 8% | 0.5 ml. | 0.5 ml. |

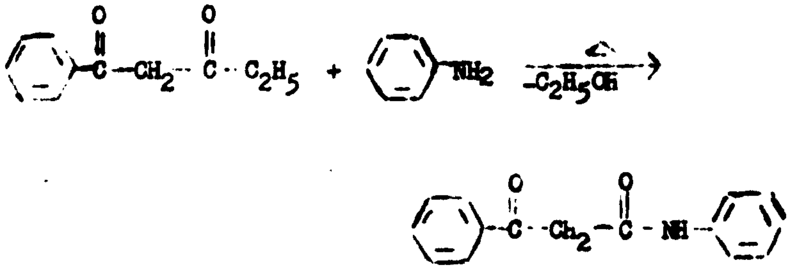
Approximate minimum exposures were determined by trial and error exposures using a 375 watt photoflood at 15 inches as the light source and processing in 1% hydrogen peroxide prior to washout with warm water. Both 177-A and 177-B were estimated to have the same minimum exposure of 15 seconds for formation of a photoresist.

When coating 177-A was processed in the following sequence -- (1) 1% $H_2O_2$, (2) wash, (3) 2% 4-amino-N-ethyl-N-(-β-hydroxyethyl)-aniline, (4) 2% ammonium persulfate-sodium carbonate -- a deep blue photoresist image was obtained. As usual with paper base coatings subjected to color development, considerable background stain was evident.

The polymeric indoaniline cyan dye presumed to be formed in the photoresist is of the following structure.

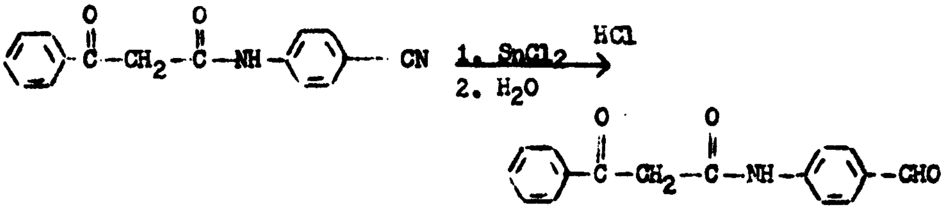


Having thus demonstrated the feasibility of this type of color former monomer, the synthesis of a benzoylacetanilide (yellow) and a 5-pyrazolone (magenta) substituted methylenebisacrylamide was undertaken. A cursory search of the color former intermediates available in the Ansco Laboratories and of the related literature failed to turn up any formyl substituted benzoylacetanilide or 5-pyrazolone intermediates for condensation with acrylamide as indicated in the general equation above. Accordingly, the synthesis of 4-formylbenzoylacetanilide was undertaken. The conventional synthesis of the benzoylacetanilide structure entails the condensation of ethyl benzoylacetate with an aniline derivative.



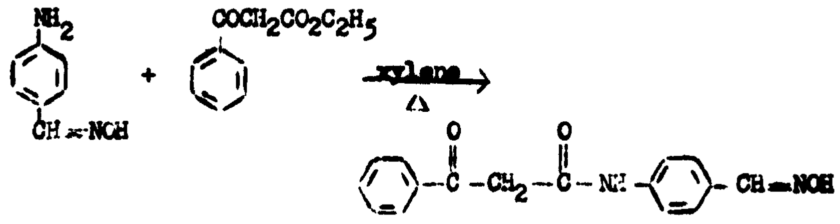
However, the straightforward preparation of 4-formylbenzoylacetanilide by condensation of ethyl benzoylacetate with 4-aminobenzaldehyde is precluded by the lack of stability of 4-aminobenzaldehyde due to its rapid intermolecular polycondensation to a resinous Schiff base. It, therefore, becomes necessary to block the aldehyde function with a group that conveniently can be removed after the acetanilide condensation. For this purpose the cyclic acetal (1,3 dioxolane) resulting from the reaction of ethyleneglycol with the aldehyde was prepared. 2-(4-Nitrophenyl)-1,3-dioxolane was prepared by the method of Hibbert and Sturrock(11) and catalytically hydrogenated to 2-(4-aminophenyl)-1,3-dioxolane using a platinum catalyst in ethanol. The amine was then condensed with ethyl benzoylacetate in refluxing xylene. 2-(4-Benzoylacetanilide)-1,3-dioxolane was obtained after recrystallization from ethanol as a yellow crystalline solid, m.p. 124°-125°. Hydrolysis of this compound under the conventional conditions for the hydrolysis of the 1,3-dioxolanes to the corresponding aldehyde (reflux with hydrochloric acid in aqueous ethanol) gave a resinous orange solid which melted over a wide range and could not be further purified. A fuchsin aldehyde test was negative, and infra-red analysis failed to indicate the presence of formyl hydrogen in the molecule.

This approach was abandoned at this point and the Stephen reduction of 4-cyanobenzoylacetanilide was attempted as indicated in the following equation:



4-Cyanobenzoylacetanilide was readily obtained by condensation of 4-aminobenzonitrile with ethyl benzoylacetate in refluxing xylene. The reduction was carried out according to the procedure of Stephen(12) and appeared to go smoothly to the formation of the imine stannic chloride complex. Hydrolysis of the complex salt with boiling water in a nitrogen atmosphere gave an orange solid which rapidly hardened to an intractable resin on keeping overnight in a vacuum desiccator.

Finally, an attempt was made to block the formyl group as the oxime which, as in the case of the cyclic acetal, should be capable of hydrolysis to the free aldehyde after the acetanilide condensation. p-Nitrobenzaldoxime was prepared by the method of Gabriel and Herrberg(13) and reduced to p-aminobenzaldoxime with ammonium polysulfide. The amine was then condensed with ethyl benzoylacetate in refluxing xylene yielding a light yellow solid, m.p. 170°-172°, presumed to be 4-oximinobenzoylacetanilide.



A negative diazotization test and the formation of a yellow dye on color development with 4-amino-N-ethyl-N-(β-hydroxyethyl) aniline corroborate the proposed structure. Hydrolysis of this product by the sulfurous acid method of Glund(14) yielded a gummy reaction product from which a pale yellow solid was isolated by extraction with hot ethanol. After two recrystallizations from aqueous ethanol a colorless solid melting at 125°-126° was obtained that gave a positive fuchsin aldehyde test.

<u>Analysis</u>: Calculated for $C_{16}H_{13}NO_3$: C, 71.81; H, 5.24
Found: (4192-35) C, 71.82, 71.90; H, 5.15, 5.03

Inasmuch as this product (4192-35) appeared to be an aldehyde and its elemental analysis is in agreement with that of 4-formylbenzoylacetanilide, the acid catalyzed condensation with acrylamide was attempted as follows: A solution of 4-formylbenzoylacetanilide (4192-35) (0.1 g., 0.37 mmol) and acrylamide (0.1 g., 1.4 mmols) in 3 ml. of ethylene dichloride containing one drop of concentrated hydrochloric acid was allowed to stand overnight and then refluxed for one hour. The pale yellow reaction product that separated on cooling was extracted with water and ether and dried in vacuo; m.p. 235°-241°. Trial color coupling tests with N-ethyl-N-(β-hydroxyethyl)-aniline in the presence of potassium persulfate failed to give a yellow dye. This failure to color develop and the extreme insolubility of the compound (dimethylformamide was the only satisfactory solvent found) make it appear unlikely that the product obtained is the desired N,N'-(4-benzoylacetamidobenzylidene) bisacrylamide. This conclusion is dependent upon the outcome of the elemental and infrared analyses currently on request.

### e. <u>Colored Polymers from Non-Diffusing Color Couplers</u>

Color coupler molecules substituted with alkali solubilizing groups and with a long chain hydrocarbon residue to render them non-diffusing have been found to be effectively trapped by the polymer matrix of a photoresist formed by the iron-peroxide catalyzed polymerization of N,N'-methylenebisacrylamide. This eliminates the necessity of using a polymerizable color coupler to render the photoresist color developable after washout. In addition, coating formulation is simplified in that such color couplers are readily soluble as their alkali metal salts and also by making it possible to use the readily available N,N'-methylenebisacrylamide as the monomer.

Initial trial coatings containing the non-diffusing color couplers of the benzoylacetanilide (yellow), pyrazolone (magenta), and phenolic (cyan) classes suffered from a lack of adhesion when coated on subbed Plestar. This condition was corrected by coating the color coupler containing formulation over a thin photopolymerizable subbing layer prepared according to the following formulation:

| | | |
|---|---|---|
| Gelatin, Atl. 10299, 15% | 25 | ml. |
| $H_2O$ | 65 | ml. |
| N,N'-Methylenebisacrylamide | 0.4 | g. |
| Ferric Ammonium Citrate, 36%, Brown | 10 | ml. |

Coatings have been prepared containing a mixture of yellow, cyan, and magenta color couplers that yield a black resist on color development. The correct ratio of the three color couplers needed to produce a neutral grey was determined by trial and error. The following formulation gave a black image on color development which had a maximum density of 1.3 when coated on Plestar base subbed with the photopolymerisable undercoat described above.

4155-167

| | | |
|---|---|---|
| Gelatin, Atl. 10299, 15% | 25 | ml. |
| $H_2O$ | 65 | ml. |
| N,N'-Methylenebisacrylamide | 0.4 | g. |
| Ferric Ammonium Citrate, 36%, Brown | 10 | ml. |
| Saponine, 8% | 2 | ml. |
| A-617, magenta c.f. | 0.2 | g. |
| A-607, cyan c.f. | 0.2 | g. |
| A-623, yellow c.f. | 0.3 | g. |

The color formers were solubilised with 6N NaOH and the final pH adjusted to 6.5 with citric acid prior to coating.

Color development was found to be best accomplished by bathing the freshly washed coating in a 2-5% aqueous solution of 4-amino-N-ethyl-N-($\beta$-hydroxyethyl)aniline followed by immersion in a 2% solution of ammonium persulfate containing 2 g. of sodium carbonate per 100 ml.

A further simplification of this system was achieved by the direct incorporation of color developer in the photopolymerisable coating, thus eliminating one of the processing solutions. No loss in speed was noted as a result of the p-phenylenediamine derivative in the coating. A second processing solution can be eliminated by combining the peroxide and persulfate baths; however, the stability of the mixed bath is limited to approximately 15 minutes due to exhaustion of the hydrogen peroxide by interaction with persulfate.

Coatings containing the proper balance of yellow, cyan, and magenta couplers yield black resist images of good optical density by this procedure. Thus the following coating formulation gave, after processing in hydrogen peroxide and alkaline potassium persulfate, a black resist which had a maximum density of 5.

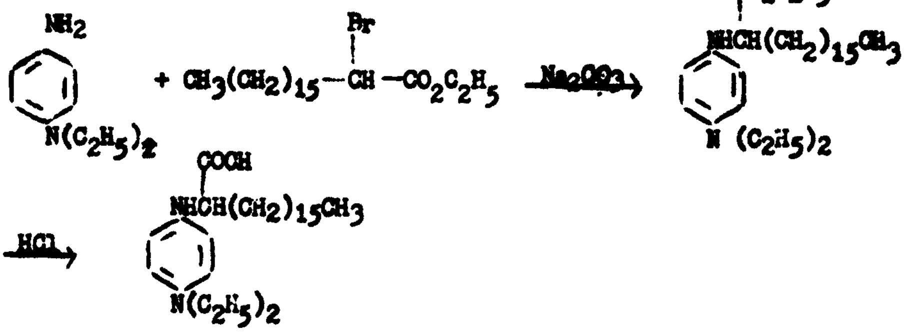
**4155-179**

| | | |
|---|---|---|
| Gelatin, Atl. 10299, 15% | 25 | ml. |
| $H_2O$ | 65 | ml. |
| MBA | 0.4 | g. |
| Ferric Ammonium Citrate, 36%, Brown | 10 | ml. |
| A-607, cyan c.f. | 1 | g. |
| A-617, magenta c.f. | 1 | g. |
| A-620, yellow c.f. | 1 | g. |
| 4-Amino-N-Ethyl-N-(β-hydroxyethyl) aniline·½$H_2SO_4$ | 3 | g. |

Sufficient 6N NaOH added to solubilize the color formers. Final pH at coating, 7.0.

The shelf life of such coatings has been found to be limited, a serious loss in color density occurring within three-five days. Some of the original density can be restored by additional color development suggesting that depletion of the color developer takes place on storage. The great sensitivity of developers of the p-phenylenediamine class to oxidative degradation is well known, and the indicated depletion in developer activity can be logically attributed to oxidation. British Patent No. 783,887 assigned to the Gevaert Photo-Producten N.V. describes a class of color developers based on the p-dialkylaminophenylglycine structure which have improved resistance to oxidation and are claimed to be particularly suitable for incorporation in conventional photographic coatings. Accordingly, it was of interest to test this type of color developer in the photopolymerizable system in hope of increasing the shelf stability.

For this purpose, 4-diethylamino-(α-carboxy-n-heptadecyl) aniline dihydrochloride was prepared via the following sequence described in the above mentioned patent. This particular homolog was selected in hope that the non-diffusability conferred on the molecule by the heptadecyl chain would minimize the loss of developer due to leach out in the hydrogen peroxide processing bath.

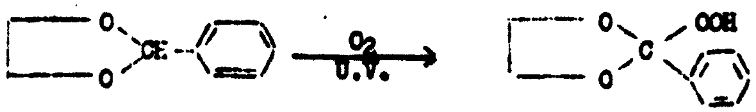


The α-bromoethylstearate used was prepared by the method of Hall and Sadomsky(19). The product was obtained as a light tan, waxy solid, m.p. 140°-150°. Reaction with the color formers used in the coating in the presence of alkaline persulfate gave the corresponding dyes very slowly. Even in solution maximum dye density was not obtained for periods up to one hour. Obviously the extremely slow rate of coupling displayed by this developer makes it unattractive for use in the photopolymerization system. In order to determine if the slow rate of color development observed is more a consequence of the size of the leaving group (the carboxyheptadecyl group is split off in the process of color coupling) than of the inherent activation energy of the cleavage process, the smaller 4-diethylamino-N'-carboxymethylaniline was synthesised. Solution experiments show this developer to color couple at a somewhat faster rate than the heptadecyl derivative but at a considerably slower rate than the 4-amino-N-ethyl-N-(β-hydroxyethyl)-aniline used initially. Coating trials were made by substituting 4-diethylamino-N'-carboxymethylaniline for 4-amino-N-ethyl-N-(β-hydroxyethyl)-aniline in coating formulation 4155-179 given above. After exposure and color development, the photoresist acquired a light green color on prolonged immersion in an alkaline persulfate solution. It was concluded that the rate of oxidation and therefore of color coupling of this type of color developer is too slow to make it practical in this system. Undoubtedly it is this same resistance to oxidation that gives this type of developer its outstanding stability.

## 4. New Photopolymerisation Systems with Increased Sensitivity

### a. Photopolymerisation Based on Autoxidation

As previously outlined in the Final Report for 15 November 1962 - 14 February 1963 under the same heading, photosensitized autoxidation can, in theory, lead to a peroxide latent image which can subsequently be activated by either light, heat, or a reducing agent to yield radicals capable of initiating polymerization. The scheme is the reverse of the iron-peroxide system with the important difference that, while the quantum yield for the photoreduction of Fe(III) to Fe(II) cannot exceed one, the chain reaction nature of photosensitized autoxidation makes large quantum yields possible. Most probably, the key to developing a practical photopolymerization system based on photosensitized autoxidation lies in finding a suitable substrate. In this regard it was of interest when, in the course of the synthesis of 4-formylbenzoylacetanilide, the 1,3-dioxolanes prepared as intermediates appeared to exhibit sensitivity to oxygen and light in much the same manner as the aromatic hydrazones previously found to be useful autoxidation substrates. A check of the literature revealed the work of Rieche et al(15), in which the ultraviolet sensitized autoxidation of 2-phenyl-1,3-dioxolane to yield a hydroperoxide is reported. As is well known, benzylic hydrogen and hydrogen alpha to ether oxygen are particularly susceptible to autoxidation. It is therefore not surprising that the benzylic hydrogen in the 1,3-dioxolane is exceedingly reactive in this respect since it is located in a benzyl position and is also alpha to two ether-like oxygen atoms.



A sample of 2-phenyl-1,3-dioxolane was prepared as follows: <u>2-Phenyl-1,3-Dioxolane</u>. A solution of freshly distilled benzaldehyde (21.2 g., 0.2 mole) and ethylene glycol (12.4 g., 0.2 mole) in 50 ml. of dry xylene containing 4 drops of concentrated sulfuric acid was distilled slowly until the distillate temperature came to 160°. The distilland was then washed with dilute $NaHCO_3$, water and dried over Drierite. Fractionation in vacuo gave 37 g. (75%) of 2-phenyl-1,3-dioxolane as a colorless oil, b.p. 70° (1 mm.), $N_D^{20}$ 1.5270.

When a solution containing several drops of 2-phenyl-1,3-dioxolane in 2 ml. of benzene was saturated with oxygen and irradiated for two minutes with ultraviolet light, sufficient hydroperoxide was generated to initiate immediate polymerization when a few drops of the autoxidized solution was added to a few ml. of A-5 solution containing a trace of ferrous ion.

The following trial coatings were prepared:

<u>Autoxidation Coatings</u>

| | <u>4155-184C</u> | <u>4192-49</u> | <u>4155-184D</u> |
|---|---|---|---|
| PVP masterbatch* | 50 ml. | 50 ml. | 50 ml. |
| 2-Phenyl-1,3-Dioxolane | 1 ml | 1 ml. | - |
| 1% Rose Bangal | - | 1 ml. | 1 ml. |

*60 g. PVP, 210 ml. ethanol, 90 ml. water, 8 g. N,N'-methylenebisacrylamide, 6 ml. dimethylphthalate, 2 ml. 10% Wetsit.

The formulations were coated on baryta paper. Coating 4192-49 gave a photoresist after 30-second exposure to the usual light source and immersion in 1% aqueous ferrous ammonium sulfate. Exposed areas not treated with the ferrous solution failed to retain a resist at this exposure level. Coating 4155-184C containing no rose bengal failed to produce a resist after a two-minute exposure. Coating 4155-184D containing only rose bengal gave a very faint resist after a two-minute exposure. Post-exposure processing of this coating appeared to enhance the resist quality slightly.

Further experimentation directed at determining the effect of concentration and structure of the 1,3-dioxolane on this system as well as other photosensitizers is currently in progress.

### b. Eder's Reaction as a Photoinitiator System

The photoinitiated reaction of mercuric chloride with potassium oxolate was first described by Eder(16) and has the following stoichiometry:

$$K_2C_2O_4 + 2HgCl_2 \xrightarrow{h\nu} Hg_2Cl_2 + 2KCl + 2CO_2$$

The following characteristics of the reaction have been demonstrated(17): (1) Reaction proceeds via a chain mechanism and with a larger than unit quantum yield. (2) No reaction occurs in the dark in the absence of photo- or chemical initiation. (3) The reaction exhibits a strong sensitivity to inhibition and catalysis--certain dyes such as eosin act as photosensitizers and oxygen acts as a strong inhibitor.

Consideration of the above reaction characteristics suggests a free radical mechanism and therefore the system was tested for photoinitiator properties. It was found that, when mercuric chloride and potassium oxalate are added to A-5 solution and exposed to ultraviolet radiation, no polymerization resulted. However, when the solution was purged with nitrogen before exposure, polymerization was initiated on short exposure. Coating trials were formulated as follows and coated on baryta paper.

<u>4192-29</u>

| | I | II | III |
|---|---|---|---|
| Gelatin, Atl. 10299, 15% | 25 ml. | 25 ml. | 25 ml. |
| $HgCl_2$, 0.2M | 10 ml. | 1 ml. | 20 ml. |
| $K_2C_2O_4 \cdot H_2O$, 1M | 1 ml. | 1 ml. | 1 ml. |
| A-5 | 3 ml. | 3 ml. | 3 ml. |
| $H_2O$ | 15 ml. | 24 ml. | 5 ml. |
| Saponine, 8% | 1 ml. | 1 ml. | 1 ml. |

None of the above coatings gave any indication of photoresist formation after exposure to a U.V. source (one 15 watt germicidal lamp at a distance of three inches) for five minutes.

The sensitivity of Eder's reaction to the blue region of the spectrum, where neither mercuric chloride nor potassium oxalate absorb, has been attributed by Cartledge(17) to the presence of impurities--notably iron. When ferric ammonium oxalate was added to a solution of mercuric chloride and potassium oxalate in A-5, polymerization could be photoinitiated even without prior removal of oxygen from the solution. Coatings (4155-181) were prepared similar to the 4192-29 formulation with the addition of 1 ml. of 36% ferric ammonium oxalate. Prolonged exposures of these coatings produced no photoresist unless the exposed coatings were bathed in dilute hydrogen peroxide prior to washout.

## 5. Miscellaneous Observations

### A. Iron-Peroxide Photopolymerization System

As suggested in the Final Report for 15 November 1962 - 14 February 1963 under the heading of Suggested Further Work (Section F-8-(f)), a program has been initiated to quantitatively evaluate the iron-peroxide photopolymerization system for the purpose of estimating how much additional speed can be realized from the system by further optimization. The initial work has had as an objective the determination of the percent conversion of monomer to polymer necessary in the N,N'-methylenebisacrylamide-gelatin system to achieve insolubilization after photoinitiation by the iron-peroxide system. This data is expected to yield insight into the efficiency of N,N'-methylenebisacrylamide (MBA) in the process and thus into the margin of improvement that could be accrued by the use of a more ideal monomer.

The analytical estimation of the decrease in monomer concentration that accompanies photopolymerization in a thin coated layer presents several problems. The conventional technique of monomer determination based on iodometric measurement of the amount of bromine consumed by addition to the unsaturation of the monomer is impractical due to the nonstoichiometric consumption of bromine by the gelatin binder. Trial and error experimentation with coating formulations containing gelatin, MBA and ferric ammonium citrate indicated that, when such formulations are coated on a nonabsorbing base such as Plestar, the minimum gel/MBA ratio necessary to prevent crystallisation of the MBA in the dried layer is about 8:3. Somewhat lower ratios can be coated on an absorbent substrate such as paper without crystallization, presumably due to imbibition of monomer by the base. Comparison of the infrared spectra of gelatin, MBA and poly-MBA (prepared by Fe(II)-$H_2O_2$ initiated polymerization of a 4% aqueous solution of MBA) revealed that MBA has several well defined absorption bands in the 10-13µ region, an area which is transparent in the poly-MBA and gelatin spectra. It is therefore theoretically feasible to determine the monomer content of a gelatin foil by quantitative infrared spectroscopy. Accordingly, a series of gelatin foils were prepared containing varied amounts of MBA and their infrared spectra recorded for the purpose of obtaining a calibration plot of optical density versus MBA concentration. However, it was found that, even at the maximum gel/MBA ratio, at least five foil thicknesses (~35µ) were required to give a measurable MBA absorption before polymerization. Furthermore, when the infrared spectrum of several foil layers was recorded, absorption due to interference phenomena associated with the surface of the foils becomes so intense that quantitative results based on absorption in the region of interest become unintelligible.

At this point, the spectrophotometric method was abandoned in favor of gravimetric estimation of the poly-MBA formed in the photopolymerization. This value combined with a knowledge of the amount of MBA present before polymerization readily gives the percent conversion of monomer to polymer. The following determination based on the insolubility of the highly crosslinked poly-MBA was developed: Small "puddle" coatings were prepared by placing a weighed amount of coating formulation on unsubbed Plestar base which had been pretreated with a 1% solution of saponine. Conditioning of the base with a wetting agent was necessary to facilitate the flow of the coating solution into round, reasonably uniform coatings. A number of such "puddle" coatings were prepared from a coating solution containing 9.7 mg. MBA/g. coating solution. When using 1.5-2.0 g. of coating solution, coatings measuring 6-8 cm. in diameter and 30-40µ thick obtained. After exposure and processing in 1% hydrogen peroxide, the polymerized layer could be easily and quantitatively stripped from the base and transferred to a beaker as a consequence of the lack of adhesion of the polymerized coating to the unsubbed Plestar base. Thus it was possible to prepare a small coating containing a precisely known weight of MBA and to quantitatively strip it from the base after exposure and processing. The stripped coating was then enzymatically degraded with Takamine and the insoluble poly-MBA collected on a sintered glass Gooch crucible, dried in vacuo, and weighed. Citric acid was added during the digestion period to insure solubilization of any tanned gelatin formed by free ferric ion resulting from oxidation of photoformed ferrous ion by hydrogen peroxide. The following table summarizes the results obtained via this procedure.

### Table VII

### Photoconversion of MBA to Poly-MBA*

| Coating | Weight, g. | Exposure, sec.** | poly-MBA, mg. | % Conversion |
|---|---|---|---|---|
| 1. | 1.5909 | 15 | 14.9 | 96.4 |
| 2. | 1.3954 | 30 | 13.7 | 101.0 |
| 3. | 2.0792 | 60 | 16.8 | 83.2 |
| 4. | 1.6013 | 120 | 11.0 | 70.5 |

*The original coating solution contained 9.72 mg. MBA/g.
**Exposures were made using a 375 watt photoflood at a distance of 15 inches.

Discussion of Table VII. The lack of correlation between exposure level and percent conversion shown by these data shed doubt on the reliability of the analytical method and underscore the need for duplicate experiments. Further than this, the impossible conversion measured for coating 2 prompted a closer look at the poly-MBA isolated via this technique. The infrared spectrum of the polymer obtained from the coated layer is practically superimposable on that of pure poly-MBA with the exception of two very weak bands at 7.55 and 12.75μ. Neither of these bands is present in the spectrum of the gelatin used in the experiment; however, a sensitive color test for protein, based on the formation of violet colored Schiff bases by reaction of p-dimethylaminobenzaldehyde with acid hydrolyzed protein(18), was positive for gelatin and polymer isolated from the photopolymerized layer but negative for pure poly-MBA. Prolonged digestion (48 hours) with Takamine and citric acid followed by thorough washing with water and alcohol failed to prevent the photopolymerized poly-MBA from giving a positive gelatin test. This result, while interesting in that it implies some chain transfer to gelatin in the polymerization process, introduces an additional variable into this method developed as a means of estimating the percent conversion of monomer to polymer.

The following PVP based formulation was similarly coated on unsubbed Plestar base and processed as in the gelatin based coatings.

### 4192-30

| | | |
|---|---|---|
| Polyvinylpyrrolidone, K-30 | 10 | g. |
| Water | 50 | ml. |
| N,N'-Methylenebisacrylamide | 1.50 | g. |
| Ferric ammonium oxalate, 36% | 5 | ml. |
| Saponine, 8% | 1 | ml. |

After exposure and processing with 1% hydrogen peroxide, the insoluble polymer was isolated and dried in vacuo. A sample was submitted for nitrogen analysis: Found: N, 11.96, 11.81; calculated for poly-MBA ($C_7H_{10}O_2N_2$), N, 18.17; for PVP ($C_6H_9NO$), N, 12.71. This experimental result obviously cannot be reconciled in terms of a graft copolymer of PVP and MBA. It may mean some hydration of the polymer; however, the low nitrogen analysis and the infrared spectrum almost certainly indicate a significant degree of chain transfer to binder. While this conclusion makes the determination meaningless for the estimation of percent conversion of monomer to polymer, it does provide a technique for the estimation of the tendency of various binders to enter into the photopolymerisation process.

## References

(1) H. Hodgson and W. Rosenberg, J.C.S., 15-18 (1930)

(2) N. J. Leonard et al, J.Am.Chem.Soc. 71, p. 2997 (1949)

(3) I. N. Somin and S. G. Kuznetsov, Zhur Obschei Khim 30, 220-227 (1960) as abstracted in C.A. 54, col. 22,483 (1960)

(4) Ghosh, Narayanmurti and Roy, Z.physik.Chem. B 29, p. 236 (1935)

(5) G. Oster, Photo.Sci.and Eng., Vol. 4, p. 176 (1953)

(6) L. E. Levi, Ber. 20, 513-7 (1887)

(7) W. A. Armstrong and G. A. Grant, Radiation Research, Vol. 8, 375-387 (1958)

(8) O. Gros, Z.physik Chem. 37, 157 (1901)

(9) N. Zelinsky, Ber. 24, 4006-17 (1891)

(10) E. E. Magat, B. F. Faris, J. E. Reith and F. Salisbury, J.Am.Chem. Soc. 73, 1028 (1951)

(11) H. Hibbert and M. G. Sturrock, J.Am.Chem.Soc., 50, 3375 (1928)

(12) H. Stephen, J.Chem.Soc., 122, 1874 (1925)

(13) S. Gabriel and M. Herrberg, Ber. 16, 2000 (1883)

(14) W. Gluud, Ber. 48, 422 (1915)

(15) A. Rieche, E. Schmitz and E. Beyer, Chem. Ber. 91, 1935 (1958)

(16) J. M. Eder, Ber. 13, 166 (1880)

(17) G. H. Cartledge, J.Am.Chem.Soc. 63, 906 (1941); G. Kornfeld, Sci.Ind. Phot., 378 (1952)

(18) O. Frehden and L. Goldschmidt, Mikrochim. Acta 1, 351 (1957)

(19) C. Hell and J. Sadomsky, Ber. 24, 2391 (1891)

## References

(1) H. Hodgson and W. Rosenberg, J.C.S., 15-18 (1930)

(2) N. J. Leonard et al, J.Am.Chem.Soc. 71, p. 2997 (1949)

(3) I. N. Somin and S. G. Kuznetsov, Zhur Obschei Khim 30, 220-227 (1960) as abstracted in C.A. 54, col. 22,483 (1960)

(4) Ghosh, Narayanmurti and Roy, Z.physik.Chem. B 29, p. 236 (1935)

(5) G. Oster, Photo.Sci.and Eng., Vol. 4, p. 176 (1953)

(6) L. E. Levi, Ber. 20, 513-7 (1887)

(7) W. A. Armstrong and G. A. Grant Radiation Research, Vol. 8, 375-387 (1958)

(8) O. Gros, Z.physik Chem. 37, 157 (1901)

(9) N. Zelinsky, Ber. 24, 4006-17 (1891)

(10) E. E. Magat, B. F. Faris, J. E. Reith and F. Salisbury, J.Am.Chem. Soc. 73, 1028 (1951)

(11) H. Hibbert and M. G. Sturrock, J.Am.Chem.Soc., 50, 3375 (1928)

(12) H. Stephen, J.Chem.Soc., 122, 1874 (1925)

(13) S. Gabriel and A. Herzberg, Ber. 16, 2000 (1883)

(14) W. Gluud, Ber. 48, 422 (1915)

(15) A. Rieche, E. Schmitz and E. Beyer, Chem. Ber. 91, 1935 (1958)

(16) J. M. Eder, Ber. 13, 166 (1880)

(17) G. H. Cartledge, J.Am.Chem.Soc. 63, 906 (1941); G. Kornfeld, Sci.Ind. Phot., 378 (1952)

(18) O. Frehden and L. Goldschmidt, Mikrochim. Acta 1, 351 (1957)

(19) C. Hell and J. Sadomsky, Ber. 24, 2391 (1891)

## E. PROGRAM FOR NEXT INTERVAL

1. Continuation of syntheses of organic acids whose ferric salts are likely to yield a colored image during photopolymer formation. Specifically, these acids include 3,5,3',5' dihydroxybenzilic acid and 1,3 dihydroxy 1,3 dimethylglutaric acid.

2. Study of reactions designed to multiply the number of radicals arising from the photodecomposition of ferric benzilate or related ferric salts. It is possible that this amplification may be achieved by means of suitable additives to the coating formulation or an extra processing step. For example, the immersion of an exposed ferric benzilate layer in hydrogen peroxide affords a supply of hydroxyl radicals in addition to the photoproduced diphenylmethoxyl radicals.

3. Experiments designed to elucidate the nature of the radicals arising from the photodecomposition of uranyl salts such as uranyl acrylate. A clarification of this mechanism could suggest means of accelerating photopolymerization with uranyl salts, such as has been attempted with methylene blue-mandelic acid.

4. The search for photopolymerization systems with increased light sensitivity will be continued. Specifically, the approach based on autooxidation will be expanded and the system utilizing the 1,3 dioxolanes as the autoxidizable substrate will be investigated in detail. Variations of the binder, photosensitizer and dioxolane structure will be examined. A study of the effect of both autoxidation accelerators and antioxidants on the system is contemplated.

## F. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

| | |
|---|---|
| **Levinos, Steven** | Project Manager |
| Education: | Polytechnic Institute of Brooklyn<br>Brooklyn, New York<br>B. S. in Chemistry 1937 |
| Employment: | Co-owner, Smith Chemical Works<br>Edgewater, New Jersey<br>1936-1938 |
| | Ansbacher-Siegle Corporation<br>Staten Island, New York<br>1938-1942 Research Chemist |
| | National Bureau of Standards<br>Washington, D. C.<br>1942-1947 Research Chemist |
| | Signal Corps Engineering Laboratories<br>Fort Monmouth, New Jersey<br>1948-1955 Chief, Photographic Branch |
| | Photo & Repro Division<br>General Aniline & Film Corporation<br>Binghamton, New York<br>1956- Manager, New Fields & Contract Research |
| Research Fields: | Pigments, radiochemistry, photographic processes, photopolymerization |
| Man Hours Devoted to This Project (14 February 1963 - 13 May 1963) | 8 |
| **Cerwonka, Edward** | Research Specialist |
| Education: | Fordham University<br>Ph.D. Organic Chemistry 1952 |
| Employment: | U. S. Testing Company<br>Hoboken, New Jersey<br>1952-1953 Research Chemist |
| | U. S. Testing Company<br>Boston, Massachusetts<br>1953-1954 Research Chemist |

Metalectro Corporation
Laurel, Maryland
1954-1957 Senior Research Chemist

Photo & Repro Division
General Aniline & Film Corporation
Binghamton, New York
1957- Senior Research Chemist

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

Man Hours Devoted to This Project (14 February 1963 - 13 May 1963) 351

<u>Millard, Frederick W.</u> Research Specialist

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

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

Photo & Repro Division
General Aniline & Film Corporation
Binghamton, New York
1960- Senior Research Chemist

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

Man Hours Devoted to This Project (14 February 1963 - 13 May 1963) 446

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; and

Dr. G. A. Wiesehahn, Research Librarian.

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

Steven Levinos

Steven Levinos
Project Manager

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

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Contract No. DA36-039 AMC-00119(E)
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