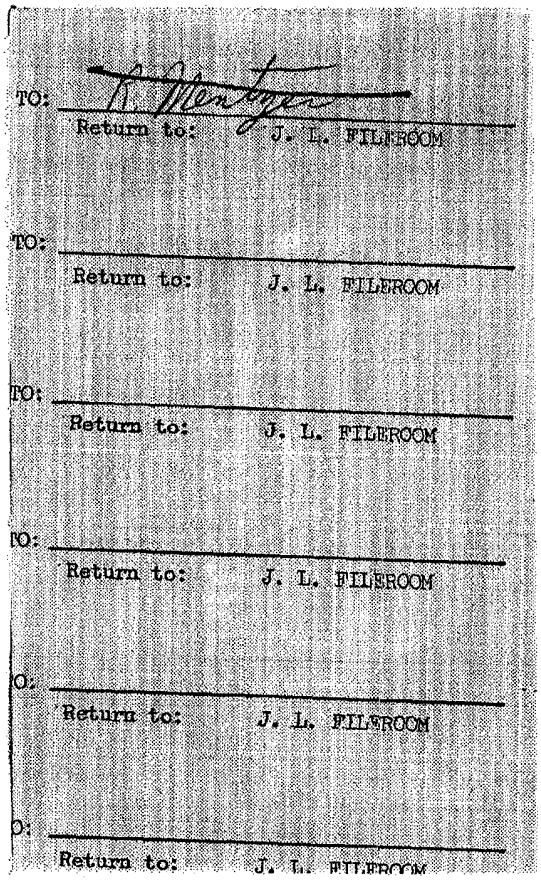
18730 (RR-53-89, no. 5)

(1) R. Mentzer 3/19/70

N37216


TO: R. Mentzer

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

O:

Return to: J. L. FILEROOM

O:

Return to: J. L. FILEROOM

DUP050040762

JLR-53-89, No. 5.

Serial Number 18730.

Dr. H. W. Elley (2)
Dr. E. K. Bolton (1)
Dr. Wm. Kirk (1)
Mr. A. J. Wuertz for I.C.I (3)
J. L. Files (2)
Dr. S. S. Rossander (1)

Please return to JACKSON LABORATORY FILES

E. I. DuPont DeNemours & Company

Jackson Laboratory

October 16, 1943

Ponsol Olive GGL

Please return to JACKSON LABORATORY FILES

Progress Report

E. C. Buxbaum

H. R. Lee,
Group Leader

S. S. Rossander,
Division Head

JLR-53-89, No. 5. Serial Number 18730.

DUP050040763

Ponsol Olive GGL
(Project No. 1775)

E. C. Buxbaum

JLR-53-89, No. 5. Serial Number 18730.

Object of the Investigation:

To determine the nature of the impurities present in Ponsol Olive GGL and from the information derived to devise ways and means of improving the fastness properties of the product. This involves as an object the preparation of a pure sample of Ponsol Olive GGL.

Period Covered by the Report:

April 27, 1943 to August 2, 1943 intermittently.

Historical Background:

Ponsol Olive GGL is prepared by condensing one mole of 1-amino-anthraquinone with one mole of 6-Bz-1-dibromo-benzanthrone through the bromine in the 1-position. The 6-bromo atom is presumed to be unattached although analyses do not show a theoretical bromine content. This anthrimide is subjected to an alcoholic potassium hydroxide fusion to effect ring-closure which gives a product containing small amounts of bromine. The exact constitution is unknown. The crude ring-closed product is then acid pasted and standardized.

Considerable variation in shade of the final color occurs in various batches and various other colors such as Ponsol Green 2BL and Ponsol Khaki 2G have had to be used in quantities as high as 16% as shading components to match the standard. While such fluctuation in shade is not a serious defect, it would be very desirable to produce a pure color which would have a consistent shade from batch to batch.

Ponsol Olive GGL is also known to be deficient in various properties, especially fastness to light, chlorine and also in the migration test and when compared to colors like Indanthrene Olive T it suffers by comparison. Any improvement in the properties of Ponsol Olive GGL would make it of added value in the competitive post-war world in which colors of superior properties such as Indanthrene Olive T will be available.

DUP050040764

Summary and Conclusions:

Progress has been made on the separation and identification of the components of Ponsol Olive GGL. A pure sample of the color has not yet been obtained.

Chromotographic studies of the anthrimide of Ponsol Olive GGL show that all condensations of 1-amino-anthraquinone with 6-Bz-1-dibromo-benzanthrone are incomplete in that varying amounts of uncondensed dibromo-benzanthrone are always present after the condensation. Since this impurity is not removed, it is carried through the caustic potash fusion which would account for some of the blue impurities in the color consisting of violanthrone or isoviolanthrone derivatives.

It has also been shown by chromatographic studies and separations of the components in the first batches of the anthrimide of Ponsol Olive GGL that these were extremely crude mixtures containing numerous components some of which appear to be the anthrimide of Ponsol Green 2BL and Indanthrene Olive T.

Separations of the crude color as currently produced in the plant definitely show our present Olive GGL to be a mixture but much more homogeneous than it has been in the past.

As prepared in the plant, the anthrimide of Ponsol Olive GGL contains intentionally, less than the theoretical amount of bromine. Attempts to prepare a compound with correct bromine by using milder conditions in the anthrimide condensation resulted in a crude mixture from which a relatively pure compound could be obtained with difficulty after several purifications.

The usual analytical methods such as determinations of nitrogen, bromine, melting point, etc. have been of little value in determining the components of the mixture which is known as Ponsol Olive GGL. Chromatographic, colorimetric and spectrophotometric methods have been of value in determining the components of this mixture.

The original line of attack still appears to be sound. We will attempt to make the purest sample possible by employing pure intermediates and at the same time attempt to identify and eliminate impurities present.

Patent Situation:

Ponsol Olive GGL is protected by U.S. 2,212,029 to DuPont, August 20, 1940. At present there are no features of the work which require patent protection or which are involved legally.

DUP050040765

Plans for Future Work:

This includes the preparation of a pure sample of Ponsol Olive GGL when pure anthrimide is obtained. We also intend to make the 6-bromo derivative of Ponsol Green 2BL which would help to elucidate the consitution of Ponsol Olive GGL since the 6-bromine atom is not always completely removed in the fusion of the anthrimide.

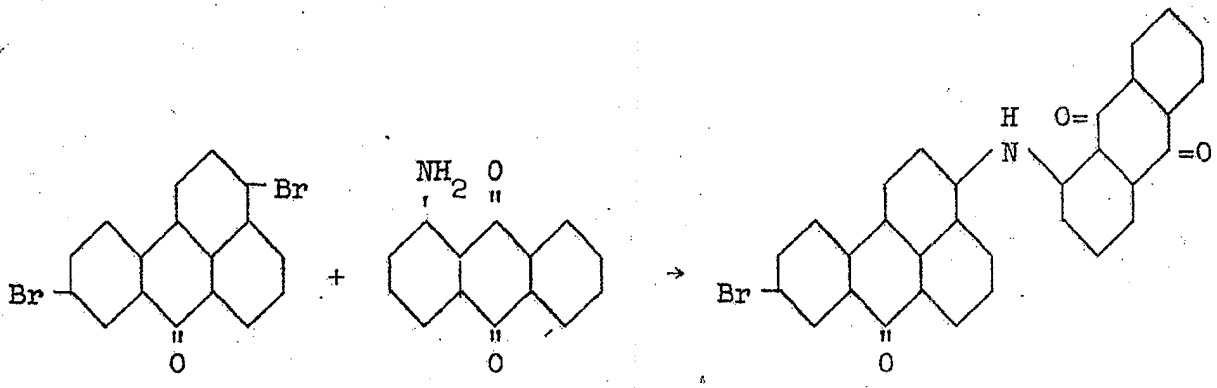
Experimental Results:

Analytical Aids

It was recognized that the usual analytical determinations of nitrogen, halogen and melting point would be of rather small value in solving this problem. The greatest use was made of the chromatograph - essentially, a column of aluminum oxide through which is passed a solution of the compound being investigated in a suitable solvent. A selective affinity separates the various components into definite bands or areas of various shade which by comparison with chromatographs of compounds of known purity can give considerable information. Photospectrometric curves were also used and color tests in sulfuric acid plus boric acid or formaldehyde were of considerable use.

Estimation of Purity of 6-Bz-1-Dibromo-Benzanthrone

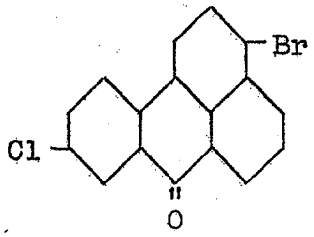
In the condensation of one mole of 1-amino-anthraquinone with one mole of 6-Bz-1-dibromo-benzanthrone, it is the Bz-1-bromine atom which is removed.



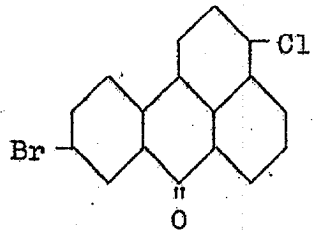
Since the 1-amino-anthraquinone is a relatively pure product whose chromatography is known, the 6-Bz-1-dibromo-benzanthrone was chromatographed. It was found that in none of the usual solvents employed was a clear definite band found, but the yellow compound was washed clear through.

DUP050040766

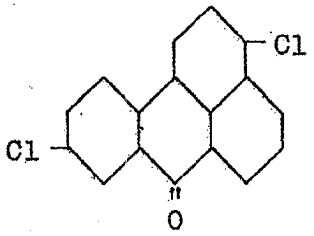
It was also found that mono-Bz-1-bromo-benzanthrone could not be separated by chromatography from 6-Bz-1-dibromo-benzanthrone by this method. However, this compound had been recently studied and a new method used to prepare it in reasonably pure form (See reference 1) . 6-Bz-1-dibromo-benzanthrone as prepared in the sulfuryl chloride-bromine-bromination as described in reference 1 may contain as high as 1.5% organic chlorine, This could mean that any one of the following compounds could be present along with the 6-Bz-1-dibromo-benzanthrone.



1

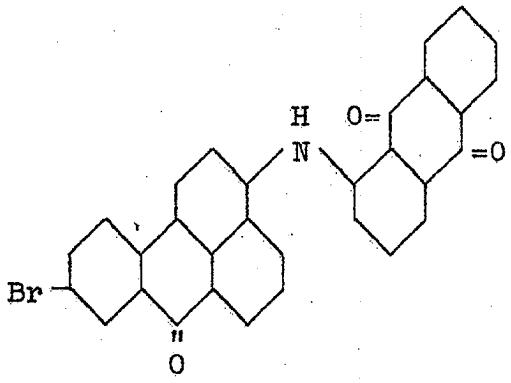


2



3

Since some of these compounds are undoubtedly present in 6-Bz-1-dibromo-benzanthrone as currently prepared, the condensation with 1-amino-anthraquinone could yield a variety of anthrimides which would not correspond to the formula of Olive GGL anthrimide as generally written.



Since the presence of 1.5% chlorine in the dibromo-benzanthrone can mean as high as 17% of a 6-chloro-anthrimide, considerable impurities are introduced at this point.

While it is assumed that the 6-halogen atom is removed in the fusion which follows, we have no right to assume that chlorine will be replaced as easily as the bromine. It is entirely possible that the fusion of the chlorine compound might result in different products from those obtained from the bromine compound.

DUP050040767

For the above reasons, it was deemed necessary to prepare a pure 6-Bz-1-dibromo compound which would contain all bromine without any chlorine. The solubility of the halogenated benzanthrones in solvents and their rapid progress through the chromatograph tube furnished a method of determining approximately the amount of 6-Bz-1-dibromo-benzanthrone left in the anthrimide after condensation with 1-amino-anthraquinone.

Ponsol Olive GGL Anthrimide (Purity)
1-(6'-Bromo-Bz-1-Benzanthronyl)-Amino-Anthraquinone

First attempts at obtaining a pure bromo-anthrimide were made by attempting solvent purifications and extractions of plant batches of the anthrimide. The first plant anthrimides obtained, however, gave chromatographs showing them to be extremely impure (JLNB-3965, pages 172, 176, 179). Several extractions in ortho-dichloro-benzene failed to give pure compounds. Some extractions gave bromine and nitrogen determinations which indicated a higher degree of purity but when these fractions or extractions were chromatographed, they were invariably crude mixtures.

Attempts were also made in the laboratory to obtain a pure anthrimide by condensing pure 1-amino-anthraquinone with 6-Bz-1-dibromo-benzanthrone, obtained from the plant. Attempts were also made to obtain a higher bromine content in the anthrimide than obtained in the plant which would be closer to the theoretical bromine, 15.1%. Since, however, the 6-Bz-1-dibromo-benzanthrone contained organic chlorine, this attempt was abandoned in favor of a condensation of pure 6-Bz-1-dibromo-benzanthrone prepared over a route that would eliminate entirely the possibility of any chlorine remaining in the molecule.

Preparation of Chlorine-Free 6-Bz-1-Dibromo-Benzanthrone

Pure 6-Bz-1-dibromo-benzanthrone was prepared by dissolving benzanthrone in five parts of bromine at 30-35°C. and stirring for 24 hours. The brominated benzanthrone was then diluted with glacial acetic acid, filtered, washed and dried (see reference 2). JLNB-4155, pages 21, 26, 38, 50.

The 6-Bz-1-dibromo-benzanthrone obtained in this manner was then dissolved in ten parts of 96% sulfuric acid and diluted with sufficient water to reduce the acidity to 84%. At this point the 6-Bz-1-dibromo-benzanthrone crystallized out and was filtered off washed and dried. In this manner, we obtained a dibromo-benzanthrone having a melting point of 260.2°C. Br 42.30. Theory 41.3.

DUP050040768

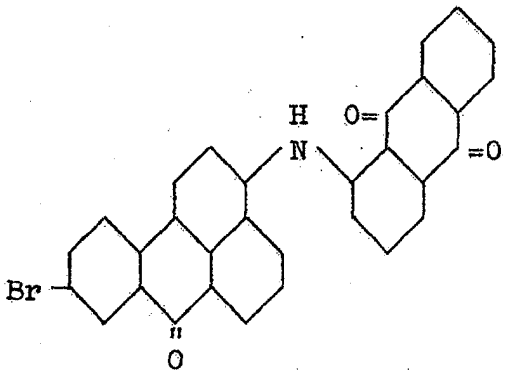
Condensations of chlorine free, acid purified 6-Bz-1-dibromo-benzanthrone were made with one mole of 1-amino-anthraquinone. JLNB-4155, pages 23, 24, 29) These were invariably impure mixtures as it appears to be impossible to condense the Bz-1-bromine atom alone and arrive at a free anthrimide without numerous purifications.

Acid Purifications of Anthrimide of Ponsol Olive GGL

Acid purification of the impure anthrimide of Ponsol Olive GGL made by condensation of chlorine free dibromo-benzanthrone with 1-amino-anthraquinone appears to offer a means of purification. JLNB-4155, page 7. In this manner, a product having the following constants were obtained. N, 2.76% - Theory, 2.64%. Bromine, 13.75% - Theory, 15.1%. M.P. 398°C.

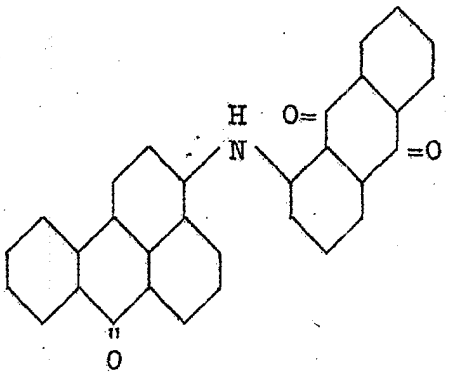
Analytical Data on Anthrimides of Ponsol Olive GGL, Ponsol Green 2BL and Indanthrene Olive T

These three compounds have the following structure in their anthrimides.



1

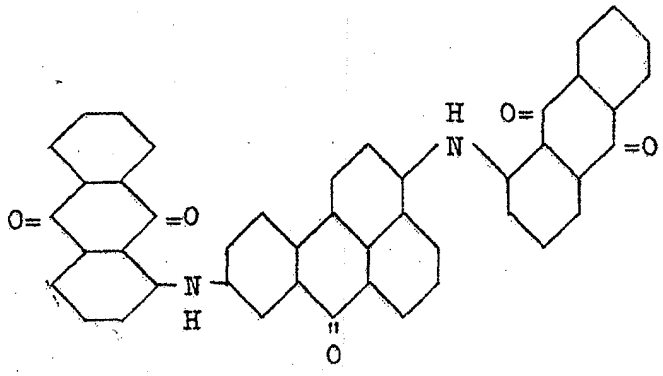
Anthrimide
Ponsol Olive GGL



2

Anthrimide
Ponsol Green 2BL

DUP050040769



3.
Anthrimide
Indanthrene Olive T

It was deemed necessary in this work to have some knowledge of the possible products of side reactions which might take place in the Olive GGL process in order to clarify the structure of Ponsol Olive GGL. Thus, a debromination of the 6-bromo atom would result in the formation of 2 or Ponsol Green 2BL anthrimide. Condensation of 6-Bz-1-dibromo-benzanthrone with two moles of 1-amino-anthraquinone would result in the anthrimide of Indanthrene Olive T, a patented product.

Chromatographic studies on the above three anthrimides show them all to be very similar in shade and inseparable from one another. Also, spectrophotometric curves showed them to give almost identical curves. However, color tests in sulfuric acid show that the anthrimide of Indanthrene Olive T gives quite a different color from the anthrimides of Olive GGL or Green 2BL, both of which are a similar color in acid. These tests were of value in identifying fractions obtained by making acid purifications of the anthrimide of Ponsol Olive GGL.

References:

1 - Tentative Dye Works Process for the Manufacture of 6-Bz-1-Dibromo-Benzanthrone Purified - C. F. Belcher, March 6, 1942.

2 - B.P. 20,837 (1906), Badische Aniline & Soda Fabrik.

3 - Purified 6-Bz-1-Dibromo-Benzanthrone - JLR-33-34, No. 2, Serial Number 17901.

4 - Purification of Vat Olives - JLR-53-108, No. 1, Serial Number 16300.

DUP050040770

5 - Alkoxy Derivatives of Ponsol Olive 2GL and Ponsol Green 2BL - JLR-53-119, No. 5, Serial Number 17441.

6 - Ponsol Olive GGL - Process Improvement and Experimental Manufacture - JLR-53-89, No. 4, Serial Number 16847.

7 - Ponsol Olive GGL - Experimental Manufacture, Lots 2 and 3.

8 - Ponsol Olive GGL - Experimental Manufacture - JLR-53-89, No. 2, Serial Number 16332.

9 - Patent Report - Supplement to AN-675.

10 - Vat Olive No. 95 - Preparation of a Final Sample - JLR-53-89, No. 1, Serial Number 16099.

11 - Patent Report - AN-675

12 - 6-Bz-1-Dibromo-Benzanthrone - Process Study JLR-33-34, No. 1, Serial Number 16846.

13 - Patent Report - AN-1135

14 - Tentative Semi-Works Process for the Manufacture of Ponsol Olive 2BL Anthrimice. W. A. Gey, September 1, 1939.

15 - Tentative Semi-Works Process for the Manufacture of 1-(6'-Bromo-Bz-1'-Benzanthronyl)-Amino-Anthraquinone.

16 - Tentative Dye Works Process for the Manufacture of 1-(6'-Bromo-Bz-1'-Benzanthronyl)-Amino-Anthraquinone

17 - Tentative Dye Works Process for the Manufacture of "Ponsol" Olive GGL Paste Crude. R. N. Lulek, December 5, 1938.

18 - Tentative Dye Works Process for the Manufacture of Ponsol Olive GGL Crude. R. N. Lulek, June 19, 1939.

19 - I.C.I. Reports - 611.13213

20 - U.S. 2,212,029, DuPont, August 20, 1940.

Submitted for typing,
November 30, 1943

Typed
December 23, 1943
emh

DUP050040771