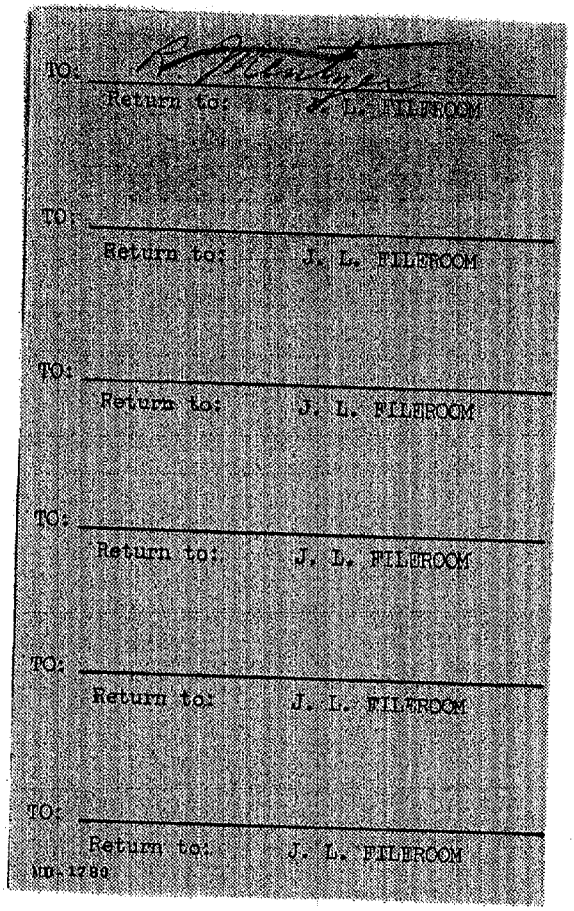
N37238



TO: [illegible]

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

TO:

Return to: J. L. FILEROOM

MM.1788

JLR-53-158, No. 3.

Serial Number 18845.

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

E. I. DuPont DeNemours & Company

Jackson Laboratory

May 25, 1944

Ponsol Olive G

Problem Report

M. S. Whelen

M. A. Perkins,
Group Leader

S. S. Rossander
Division Head

Serial Number 18845.
JLR-53-158, No. 3.

Ponsol Olive G
(Project No. 2291)

M. S. Whelen

JLR-53-158, No. 3. Serial Number 18845.

Object of the Investigation:

1 - To prepare a pure sample of Ponsol Olive G for quality tests.

2 - To improve the quality of Ponsol Olive G by an economic process.

Period Covered by the Report:

June 28, 1943 to May 25, 1944, intermittently.

Historical Background:

The manufacture of Ponsol Olive G was commenced in 1932 and since that time changes in the process have been made with a resultant change in the quality of the color obtained. In 1941, due to exigencies of production two major variations in the process were made, wherein the dibromo-pyranthrone obtained by the bromination of pyranthrone in nitrobenzene with sulfuryl chloride was isolated by steaming instead of by filtration, and this steamed product was condensed in nitrobenzene with α-amino-anthraquinone and the color isolated by steaming. The previous process had condensed the filtered dibromo-pyranthrone in naphthalene with α-amino-anthraquinone, and the color was isolated by diluting with ortho-dichloro-benzene followed by filtration. The new product so obtained was inferior to that previously produced and the yields were higher. This quality inferiority showed up in that more Jade Green had to be added to reach standard shade. On color so produced complaints were received from the textile mills that a so-called "red stain" was produced as an overcast on the surface of dyed goods.

Ponsol Olive G as produced previously to the above changes was known to be much redder and somewhat poorer in bleach and light fastness than material prepared from highly pure dibromo-pyranthrone (JLR-53-158, No. 2, Serial Number 18642).

Conclusions:

The object of the investigation was partially attained. The following conclusions were reached.

1 - Pure material has a slight advantage over standard material, being greener in shade and slightly better in light and bleach fastness, but has still less advantage over material prepared with high quality sulfuryl chloride. Preparation of the pure compound is too expensive to constitute a feasible process.

2 - The use of an improved quality sulfuryl chloride, in the bromination of the intermediate, dibromo-pyranthrone, leads to Ponsol Olive G of light and bleach fastness equal to the pure compound, but redder in shade so that it requires shading with Ponsol Jade Green to match standard shade.

3 - Red staining material encountered in manufacture by a process involving no solvent filtrations, can be removed by extraction with ortho-dichloro-benzene, but at a weight loss of 25% and an over-all tinctorial loss nearly as great (because this red material and Jade Green blend to give more "Olive G").

Recommendations:

It is recommended that pyranthrone be brominated in nitrobenzene using the highest quality sulfuryl chloride available (for oxidation of the hydrobromic acid formed to bromine), and then filtered from the solvent followed by washing and isolation in the usual manner, and then condensed with α-amino-anthraquinone in the presence of naphthalene and the color isolated by filtration from a hot naphthalene-ortho-dichloro-benzene mixture followed by steaming.

Summary:

A process study of the preparation of dibromo-pyranthrone by brominating pyranthrone with bromine and sulfuryl chloride was made. To secure good quality material it was necessary to filter off the product after bromination. It was further shown that high quality sulfuryl chloride was necessary to give best results.

The tentative specifications set up for high quality sulfuryl chloride (see experimental part) correspond to the specifications for Hooker Electro-Chemical Company sulfuryl chloride, but supplies available at Chambers Works normally fail to meet these specifications and often contain sulfuric acid which is deleterious (the mass must be kept anhydrous during bromination for the same reason) causing the formation of a different isomeric dibromo-pyranthrone. This isomer when condensed with 1-amino-anthraquinone gives rise to a brown dyestuff rather than the desired olive. When condensed with α-amino-anthraquinone gives rise to a brown dyestuff instead of an olive.

A process study of the preparation of the color was made and it was shown that condensation of dibromo-pyranthrone with α-amino-anthraquinone in naphthalene followed by dilution with ortho-dichloro-benzene and a hot filtration, similar to the original process employed gave the best quality color.

A study was made to determine the cause of "red stain" on dyed piece goods, when impure color was utilized. This was due to the impurities left in the color when filtration was eliminated. A method of extracting the crude color with ortho-dichloro-benzene with a resultant weight loss of 25% was worked out, and introduced, as an expedient, to plant production. It satisfactorily eliminated the staining material.

A very pure sample of dibromo-pyranthrone, free from chlorine, was prepared by brominating pyranthrone with bromine only, followed by repeated crystallization from sulfuric acid, until nearly the theoretical content of bromine was obtained in the product. This material was converted to color, and a color much greener in shade than unshaded Ponsol Olive G (Ponsol Olive G is normally shaded with about 4% Jade Green Double Paste), and having a trace to noticeably better bleach fastness, and noticeably superior light fastness was obtained. It is to be noted that the bleach and light fastness though improved over standard is not better than that obtained when pure sulfuryl chloride was used.

Patent Situation:

No new patentable features are involved and the patent situation is unchanged.

Experimental

A - Ponsol Olive G Crude

1 - Removal of Impurities Causing "Red Stain"

A composite sample of Ponsol Olive G Crude (steamed material) Charges 249, 250 and 251, 80 mesh, was extracted by heating at 175°C. in ortho-dichloro-benzene for two hours, followed by filtration at 100°C., washing with ortho-dichloro-benzene at 100°C. and steaming of the cake to remove solvent. The following recovery was obtained. JLNB-4059, pages 148, 149.

Table 1

No.	Parts O.D.C.B	% Recovery
148-1	12	74.0
148-2	12	74.0
148-3	8	70.6
148-4	6	78.4
148-4-R	Steamed filtrate	17.6

Samples 148-1 and 148-2 and the crude unextracted material 149, were acid pasted and made up to 11.9% gross solids, which is the same as Ponsol Olive G standard extracted solids (Gross 13%) and dyed on this basis. Since Ponsol Olive G is shaded with Ponsol Jade Green, it was necessary to make shadings with 2% Ponsol Jade Green Double Paste combined with 1% Ponsol Golden Orange G.

The following results were obtained:

Table 2

vs. Ponsol Olive G Standard 11.9% Extracted Solids

11.9% Paste	Strength on Skeins	Shade on Skeins	Strength on Pads	Shade on Pads	With 2% Jade Green and 1% Golden Orange G Skeins	With 2% Jade Green and 1% Golden Orange G Pads	Light Fastness	Bleach Fastness 0.3% Chlorine	Bleach Fastness 0.7% Chlorine
148-1	115/100	con. redder notic. duller	125/100	con. redder notic. duller	105/100 notic. red trace dull	105/100 similar	Similar as is and when shaded	trace inferior	similar
148-2	115/100	con. redder notic. duller	125/100	con. redder notic. duller	105/100 notic. red trace dull	105/100 similar	Similar as is and when shaded	Similar	trace inferior
149	140/100 (unextracted crude)	much redder apprec. duller	137/100	much redder apprec. duller			similar	notic. superior	notic. superior
148-4-R Steamed filtrate	Very weak	pinkish	taupe shade				moderate to poor	moderate	

JLNB-4059, pages 148 and 149.

No red staining could be observed on dyeings made from the extracted samples when padded on piece goods. As an expedient, extraction of the crude material in the plant was carried out using 8 parts of ortho-dichloro-benzene and a resultant weight loss of 25% was experienced. The color so obtained was found to be free from red staining material and was considered to be of satisfactory quality. On standardization, however, it was found that only 2% of Ponsol Jade Green Double Paste was necessary to shade it to standard shade as compared to about 4-5% used in the standard and a further lowering of the tinctorial yield of about 20% was experienced. It was felt that this further loss had something to do with the removal of the red component in that the red impurity, while it had little tinctorial value in itself, might build-up with Ponsol Jade Green to give tinctorial strength. Accordingly, a further series of experiments was made and the results set forth below were obtained. To avoid confusion between gross and extracted solids, since in the analytical method used to obtain an extracted solids value, most of, though not all, the red component impurity is removed, it was found necessary to make all comparisons on a weight basis.

Experiment 42-1

24 Grams Ponsol Olive G Crude, composite charges 249, 250, 251 was dissolved in 250 grams 98% sulfuric acid, poured into water and the dyestuff filtered off and washed free from acid. This was made up to 200 grams paste, extracted solids 10.72%.

Experiment 42-2

48 Grams Ponsol Olive G Crude, composite charges 249, 250 and 251 was extracted with 384 grams ortho-dichloro-benzene, filtered at 100°C. and the cake washed with ortho-dichloro-benzene at 90°C. and then steamed and dried (42-2), yield 37 grams, being a recovery of 77.0%. The filtrate was steamed and 8 grams (42-2-R) of material was obtained, being 17% of the weight of crude dyestuff taken.

18.5 Grams of 42-2, (equivalent to 24 grams crude color) was acid pasted, made up to 200 grams paste; extracted solids 8.80%.

7.5 Grams of the residue (42-2-R) was made up to 75 grams paste. Gross solids 10.2%; extracted solids 3.85%. On the gross solids basis, this dyed about 600/100 vs. Ponsol Olive G Standard, the shade being a pinkish taupe.

The following comparative dyetests were made on a weight basis:

42-1 - 116/100, much redder and noticeably duller vs. Ponsol Olive G standard
42-2 - 142/100, much redder and noticeably duller vs. Ponsol Olive G standard
42-2 is 120/100, noticeably greener vs. 42-1; 77 parts 42-2 and 23 parts 42-2-R, dyed 120/100 noticeably redder vs. 42-1.

On shading a mixture of 95.5 parts 42-1 and 4.5 parts Ponsol Jade Green Double Paste was 100/100, appreciably bluer vs. Ponsol Olive G Standard, and a mixture of 98 parts 42-2 and 2.0 parts Ponsol Jade Green Double Paste dyed 134/100 appreciably bluer vs. Ponsol Olive G standard. The red component 42-2-R when mixed with Ponsol Jade Green in ratio of 97 to 3, gave an olive shade not too far different in shade from Ponsol Olive G standard in a strength of about 600/100. JLNB-4257, pages 42-43.

An analysis of these results showed that tinctorial loss was encountered, because less Ponsol Jade Green Double was utilized for shading the extracted color than color crude. The extracted color utilized about 2% of Ponsol Jade Green Double, while the crude color containing red impurity usually takes about 4-5% of Ponsol Jade Green Double Paste.

Ponsol Jade Green built up with the red impurity to give good tinctorial value in the olive shade.

B - Dibromo-Pyranthrone - A study of its preparation.

It is an established fact that to secure the correct isomer of dibromo-pyranthrone suitable for the preparation of Ponsol Olive G, bromination of pyranthrone with bromine must be carried out in a solvent such as nitrobenzene in the absence of sulfuric acid. Bromination in the presence of sulfuric acid gives rise to a dibromo-pyranthrone, which when condensed with α-amino-anthraquinone yields a brown dyestuff. The process employed has involved bromination in nitrobenzene by adding four atoms of bromine per mole of pyranthrone and then adding sulfuryl chloride and isolating the dibromo-pyranthrone by filtration. This filtration is difficult, and due to exigencies of production steaming of the whole reaction mass was resorted to with a resultant lowering in quality. The product obtained is usually about 20% too high in halogen, a typical example being Charge 379; bromine, 22.18%; chlorine, 6.21%, which is equivalent to a total bromine content of 35.68% (theory bromine in dibromo-pyranthrone 28.4%). It had previously been the custom to condense filtered dibromo-pyranthrone with two moles of α-amino-anthraquinone in naphthalene. This was diluted, after the condensation, with ortho-dichloro-benzene and the dyestuff filtered off.

This was again a poor filtration, so to get out production the condensation was made with steamed dibromo-pyranthrone in nitrobenzene and the product was isolated by steaming the reaction mass. A much inferior product, containing all the impurities was obtained in increased yield. It contained reddish dyeing impurities, which gave trouble in the mills due to the previously described "red stain" as an overcast on piece goods.

1 - Purification by Crystallization from Sulfuric Acid

A composite of dibromo-pyranthrone was prepared from four plant charges.

Charge 382 - Bromine 22.40 - Chlorine 3.85
Charge 378 - Bromine 22.41 - Chlorine 6.21
Charge 380 - Bromine 22.06 - Chlorine 5.49
Charge 379 - Bromine 22.18 - Chlorine 6.21

40 Grams of the above was dissolved in 600 grams 97.2% H_2SO_4 and slowly diluted with water to the strengths shown below. The precipitated dibromo-pyranthrone was filtered off, filtrations being extremely poor, the product being hair-like blue needles. It was washed with acid of the same strength as the mother liquor, until clear and then slurried in hot water, filtered and washed. The following results were obtained.

Table 3

No.	Filtered from	% Recovery	Analysis % Bromine	Analysis % Chlorine
136-1	92% H_2SO_4	67.5	25.00	2.97
136-2	91% H_2SO_4	70.7	24.48	3.54
136-3	90% H_2SO_4	70.7	24.23	3.78
136-4	89% H_2SO_4	70.7	23.88	3.72
11-1	91% and then 96% H_2SO_4	39.5	25.27	3.28
11-2	91% H_2SO_4	65.0	23.37	3.86
Material from 11-1 and 11-2 combined				
11-C	92% H_2SO_4	93.5	25.66	2.70
11-C Recrystallized				
11-CP	96.5% H_2SO_4	76.4	25.53	2.33

Further experiments using methyl alcohol and acetic acid as diluent and also digesting in 91% H_2SO_4 at 65°C. were carried out with no improvement in filtration or quality.

JLNB-4059, pages 136, 137, 139
JLNB-4257, page 11

The above products when condensed with α-amino-anthraquinone in naphthalene followed by filtration, gave color greener and brighter in shade than that obtained from the crude dibromo-pyranthrone but it showed no improvement either in bleach fastness or light fastness over that obtained from the crude.

At a later date it was found that if dibromo-pyranthrone was stirred with 96.5% sulfuric acid, crystallization took place. Dibromo-pyranthrone separated as dense orange colored crystals which gave good filtrations. From 10 parts of 96.5% sulfuric acid, a recovery of 49.3%, having a bromine content of 25.82% and chlorine content of 1.19% was obtained; while from a duplicate experiment a recovery of 60% with bromine 25.03% and chlorine 1.98% was obtained. This was from the composite of plant charges above described. It is to be noted that the chlorine content is lowered appreciably with a much better total halogen content as bromine obtained. The residues in the filtrates were isolated, and crystallization of them was again attempted by stirring in 96.5% H_2SO_4. No crystallization took place, but on dilution to 91% H_2SO_4, typical hair-like blue needles were

obtained. Both material from 96% H_2SO_4 and the crystallized filtrates from 91% H_2SO_4 gave Ponsol Olive G, the former giving material only equal to standard, while the latter was red and slightly dull. Due to low yields and very little improvement in quality the method was not considered practical.

JLNB-4257, page 36.

2 - Purification by Extraction

Purification of the composite of dibromo-pyranthrone plant crude was made by extraction with ortho-dichloro-benzene at 175°C. The recovery was 82%. This material gave color dyeing 100/100 trace to noticeably green, trace to noticeably bright vs. Ponsol Olive G standard when prepared in naphthalene followed by filtration. JLNB-4059, page 145. This improvement indicated that it was necessary to use both filtered dibromo-pyranthrone and filtered color to obtain good quality. The study of the bromination which follows was accordingly undertaken.

3 - Bromination of Pyranthrone

The method in use for the bromination of pyranthrone consists in adding four atoms of bromine per mole of pyranthrone suspended in nitrobenzene at room temperature in the presence of aniline. A dark addition product is formed. When this is complete, sulfuryl chloride is added and the whole heated 6 hours at 65°C. and 6 hours at 100-105° The normal procedure is to filter the dibromo-pyranthrone off, though at present it is isolated by steaming of the whole mass.

Many experiments were carried out with modified procedure and the following points were determined.

1 - The reaction mass must be anhydrous.

2 - Use of four atoms of bromine per mole of pyranthrone is necessary.

3 - It is necessary to form the dark colored complex with bromine at a low temperature before heating or before addition of sulfuryl chloride.

4 - A catalyst such as aniline is necessary.

5 - Nitrobenzene or ortho-nitro-toluol are suitable solvents.

6 - Heating to 190-200°C. in nitrobenzene gives a more crystalline form which filters well, but which shows no great im-

provement over material filtered at 100°C.

7 - Filtration of the bromination mass gives a better product in that it removes a red component and other impurities, and gives a product with a more satisfactory halogen content; the filtrate containing a very highly halogenated material.

8 - High quality pyranthrone gives a better dibromo-pyranthrone.

9 - Sulfuryl chloride of high quality, being particularly free from sulfuric acid gives improved dibromo-pyranthrone. Excess of sulfuryl chloride is to be avoided to prevent too much chlorination. JLNB-4059 and JLNB-4257.

With these points established a procedure, which does not differ materially from that originally introduced to production, was found to be the most satisfactory (Experiment No. 46).

50 Grams pyranthrone was suspended in 750 grams nitrobenzene and the whole was dehydrated by heating to 150°C. for one hour. The suspension was cooled to 25-35°C. and 3 grams of aniline was added followed by 40 grams of bromine over 15 minutes with good agitation.

The reaction was slowly heated to 50°C. and held 1/2 hour at the end of which time the formation of the dark colored addition product was complete.

51 Grams of freshly distilled sulfuryl chloride* was added, the reaction was heated to 65°C. and held 8 hours, to 85°C. over 2 hours and then at 105°C. for 4 hours. The dibromo-pyranthrone was filtered off, washed clear with nitrobenzene and either washed with alcohol or steamed. In either case a bright bluish-red product was obtained. Yield 61 grams. Chlorine 2.80% equivalent to 6.3% bromine, bromine 23.60%. Total as bromine 29.90% (Theory 28.4%). JLNB-4257, page 46.

*Tentative specifications for sulfuryl chloride were set up as follows:

1 - B.P. 68.0-69.5°C.

2 - Not over 10% boiling below 69°C.

3 - Dry point 69.5°C.

4 - At least 85% boiling 69.0-69.4°C.
JLNB-4257, page 127.

Sample 38-2 was recrystallized from 8 parts of 96.5% sulfuric acid with a recovery of 56.2%. Bromine 25.31%, chlorine 1.38%, total as converted to bromine 28.31% bromine. The object was to secure as high grade material as possible for preparation of high quality Ponsol Olive G. This sample gave color which dyed 100/100, trace bright vs. Ponsol Olive G standard, and as such showed much greener shade than the crude material which is always shaded with about 4% Ponsol Jade Green Double Paste to produce the standard. Bleach and light fastness were trace to superior to the standard. JLNB-4257, page 43.

Sample No. 66 was converted to color. It dyed 100/100 much redder, noticeably duller vs. the standard, with chlorine fastness a trace to noticeably superior and light fastness noticeably superior. As such it was probably about the same in shade as the unshaded standard material and was somewhat improved in its fastness properties JLNB-4257, page 87.

4 - Preparation of Pure Samples of Dibromo-Pyranthrone and Ponsol Olive G therefrom

It was previously known that to secure a pure sample of dibromo-pyranthrone it was necessary to brominate pyranthrone in nitrobenzene at a high temperature without use of sulfuryl chloride. Such a sample was previously prepared by securing a partially brominated pyranthrone which was purified by nine recrystallizations from sulfuric acid to give a bromine content near the theoretical. This sample gave Ponsol Olive G, much greener, 10% stronger, noticeably brighter, and trace to noticeably superior in bleach and light fastness when compared to Ponsol Olive G standard. It was decided to re-evaluate this type of sample to determine what improved properties a highly pure sample of color would exhibit.

Pyranthrone was suspended in nitrobenzene containing a small amount of aniline as a catalyst. An equal part of bromine was added at room temperature and after stirring two hours at 50°C. under reflux, heating was continued until 185°C. was reached after twelve hours and this temperature was held 4 hours. The reaction mass was cooled to room temperature and a fifth of a part of bromine was added and the reaction was heated slowly to 185°C. and held 12 hours. The mass was filtered at 185°C. and the product isolated. Bromine 19.1% and on a duplicate experiment it was 19.46%, after recrystallization from 91% sulfuric acid the bromine contents were 22.64 and 20.81% respectively. These samples were combined and recrystallized from 96.5% sulfuric acid.

1st recrystallization from 96.5% H_2SO_4 - Bromine 25.88%
2nd recrystallization from 96.5% H_2SO_4 - Bromine 26.31%
3rd recrystallization from 96.5% H_2SO_4 - Bromine 27.76%

66.8 Grams of dibromo-pyranthrone, bromine 27.76% was obtained from 250 grams pyranthrone. The yield of purified product being 25.7%. JLNB-4257, pages 40, 48, and 76.

This material was condensed (1 mole ratio) with a highly pure sample of α-amino-anthraquinone (2 mole ratio) in naphthalene and the color isolated by filtration from the naphthalene after dilution with ortho-dichloro-benzene. Yield 90.0%. Bromine content 4.57%. This material was acid pasted and converted into a 10.90% extracted solids paste. On an equal solids basis it dyed 90/100 much greener, noticeably brighter on skeins, and 100/100, considerably greener, noticeably brighter on pads vs. Ponsol Olive G standard. In bleach fastness it was a trace to noticeably superior, and in light fastness noticeably superior to standard. This is in agreement with highly pure material previously prepared and represents Ponsol Olive G of maximum quality. It is not greatly improved in its bleach and light fastness over material made from less pure dibromo-pyranthrone.

The process utilized for the condensation of dibromo-pyranthrone with α-amino-anthraquinone will give standard shade material when carried out in naphthalene and the color filtered off. The use of nitrobenzene tends to give redder shades (JLNB-4059, page 160), and inasmuch as filtrations from nitrobenzene are very difficult, steaming of the solvent gives an impure product containing the so-called "red stain". To remove this a filtration after condensation is essential and the use of naphthalene is preferable. By any method employed the dyestuff still contained four or more percent bromine.

Literature:

1 - Carrollville process for the manufacture of Dibromo-Pyranthrone OG, dated May 24, 1935 (dibromo-pyranthrone isolated by filtration).

2 - Dye Works process for the manufacture of Dibromo-pyranthrone OG, approved April 26, 1940 (dibromo-pyranthrone isolated by steaming)

3 - Tentative Dye Works process for the manufacture of Dibromo-Pyranthrone OG, approved October 29, 1942 (dibromo-pyranthrone isolated by steaming)

4 - Dye Works process for the manufacture of Dibromo-pyranthrone OG, approved December 28, 1943 (dibromo-pyranthrone isolated by

steaming)

5 - Dye Works process for the manufacture of Ponsol Olive G Crude, approved March 5, 1940 (uses naphthalene as solvent and filters off product).

6 - Tentative modification to Dye Works process for the manufacture of Ponsol Olive G Crude, approved March 5, 1940. (Uses nitrobenzene as a solvent and filters off product)

7 - Chambers Works process for the manufacture of Ponsol Olive G Crude approved May 5, 1944 (Uses nitrobenzene as solvent and isolates color by steaming)

Submitted for typing
August 25, 1944

Typed
August 30, 1944
emh