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Serial Number 18706

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E. I. DuPont DeNemours & Company

Jackson Laboratory

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# Ponsol Khaki 2G

## Problem Report

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# Ponsol Khaki 2G
## (Project No.2259)

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JLR-53-152, No. 2. Serial Number 18706.

Object of the Investigation:

To prepare highly pure samples of pentanthrimide carbazole (Ponsol Khaki 2G) and tetranthrimide khaki (Caledon Khaki R) and to evaluate them versus Ponsol Khaki 2G and Caledon Khaki R.

Period Covered by the Report:

February 8, 1943 to August 30, 1943.

Historical Background:

The manufacture of Ponsol Khaki 2G was commenced in 1932 and since that time variations have always been encountered in the quality of the color produced relative to shade, strength, and fastness. Some of these variations were obviously directly related to the quality of the intermediate, especially 1:4:5:8-tetra-chloro-anthraquinone which at times probably contains 1:4:5-tri-chloro-anthraquinone, and gives rise to a mixture of tetra- and penta-anthrimide carbazole. It was accordingly deemed advisable to prepare highly pure samples of 1:4:5-trichloro-anthraquinone and 1:4:5:8-tetra-chloro-anthraquinone and to convert them to the tetranthrimide carbazole (Caledon Khaki R) and pentanthrimide carbazole (Ponsol Khaki 2G), obtaining these products as pure as possible, and to compare and evaluate them versus the present standards.

Conclusions:

The object of the investigation was attained. Highly pure samples of tetranthrimide carbazole and pentanthrimide carbazole were prepared and submitted to the Technical Laboratory for evaluation as preliminary samples J-53-P-57 and J-53-P-56, respectively. From the data obtained it has been shown that (1) highly pure Ponsol Khaki 2G is 20% stronger tinctorially, and is greener and brighter than the present standard Ponsol Khaki 2G, but its fastness properties are not improved, (2) that tetranthrimide carbazole is an equally good dyestuff, and from this it is concluded that its possible presence in Ponsol Khaki 2G by way of 1:4:5-trichloro-anthraquinone in 1:4:5:8-tetra-chloro-anthraquinone is not disadvantageous.

Summary:

Tetranthrimide Carbazole (Caledon Khaki R)

A highly pure sample of 1:4:5-trichloro-anthraquinone was prepared and condensed with three moles of purified α-amino-anthraquinone. The resultant tetranthrimide was filtered from hot nitrobenzene and then converted to color by aluminum-chloride-sodium-chloride fusion and the color purified by acid oxidation followed by a partial vatting procedure. This material dyed much redder, trace duller, 100/100, on equal solids basis, vs. Ponsol Khaki 2G Standard, Lot 325, and was a trace superior in bleach fastness, and trace to noticeably inferior in light fastness versus this standard.

Pentanthrimide Carbazole

A highly pure sample of 1:4:5:8-tetra-chloro-anthraquinone was prepared by subjecting good quality material to an acid and solvent crystallization. This was condensed with four moles of purified α-amino-anthraquinone and converted to purified color in a manner analogous to that shown above. This material dyed 80/100, on an equal solids basis, much greener and noticeably brighter versus Ponsol Khaki 2G standard, Lot 325, and was appreciably inferior in bleach fastness and light fastness when compared to this standard.

Patent Situation:

No new patentable features are involved.

Experimental:

Purification of α-Amino-Anthraquinone

α-Amino-anthraquinone as produced in the plant was suspended in five parts of nitrobenzene together with 0.1 parts of charcoal. The whole was heated to 150°C. and held 3 hours and then filtered hot. The filtrate after standing overnight was filtered to remove the crystallized α-amino-anthraquinone, which was washed with .2 parts of nitrobenzene followed by .2 parts of alcohol. The cake was then slurried in 3-1/2 parts of alcohol, and the suspension filtered, after which the cake was washed with 0.2 parts of alcohol and dried. The recovery was .8 - .85 parts.

Chromatograph analysis of this product showed that almost all 1:2-diamino-anthraquinone impurity and some of the β-amino-anthraquinone impurity was removed.

This solvent method of purification was found to be a more satisfactory method of purification than one involving crystallization from 80% sulfuric acid.

JLNB-4088, pages 12, 18, and 19.
JLNB = Jackson Laboratory Notebook

Purification of Plant Solvent Processed 1:4:5:8-Tetra-Chloro-Anthraquinone and Preparation of a Pure Sample

1 - Acid Purification

200 Grams 1:4:5:8-tetra-chloro-anthraquinone (solvent processed) and 1200 grams 100% sulfuric acid (chlorine 39.50%, melting point 349-353°C.) were stirred together at 50°C. for 3-1/2 hours, then for 1/2 hour at 25°C. The insoluble tetra-chloro-anthraquinone was filtered off, and the cake washed with 96% sulfuric acid, after which it was slurried in hot water, filtered, washed and dried.

Yield - 188 grams, which is a recovery of 94%. The filtrate was drowned; 4.4 grams of material isolated. The purified material had the following analysis:

Chlorine - 40.65% - The theoretical chlorine content of 1:4:5:8-tetra-chloro-anthraquinone is 41.0%.
M.P. - 351-354°C.

The material recovered from the filtrate, showed a chlorine content of 15.93% and a melting point of 268-307°C.

2 - Solvent Purification

A composite of 450 grams of acid-purified 1:4:5:8-tetra-chloro-anthraquinone, purified as above, was dissolved at 215-220°C. in 3125 grams trichloro-benzene. Crystallization was effected by stirring while cooling to 40°C., and the tetra-chloro-anthraquinone was filtered off after standing overnight, after which it was washed with alcohol and dried.

Recovery - 430 grams = 95.5%.

Analysis - Chlorine, 40.72%, 40.96% - M.P. 354.2-355°C.

JLNB-4083, pages 10 and 11. This material was used for all subsequent preparations of pentanthrimide.

Pentanthrimide

To secure a high quality anthrimide it was necessary to filter it from the solvent and the following procedure was utilized.

22.5 Grams 1:4:5:8-tetra-chloro-anthraquinone, M.P. 354-355°C., Cl = 40.69%, 58.0 grams α-amino-anthraquinone purified, 327.0 grams nitrobenzene, 25.0 grams soda ash, 3.0 grams copper acetate and 0.3 grams copper powder were heated at 205-208°C. for five hours. The pentanthrimide was filtered from the solvent at 150°C., and it was washed with nitrobenzene and alcohol, after which it was steamed, acidified with dilute hydrochloric acid, filtered, washed, and dried. Yield 62.1 grams (87.4%). The filtrate was steamed and 10.1 grams of material was recovered. Analysis for duplicate experiments were

1 - Nitrogen - 5.08% - Chlorine - 0.54%
(On the residue 4.59% - Chlorine 1.39%

2 - Nitrogen - 5.00% - Chlorine - 0.54%
(On the residue 4.63% - Chlorine 2.08%

The theoretical content of nitrogen in pentanthrimide is 5.13%.

JLNB-4088, page 23.

A further experiment, material from which was used to prepare pentanthrimide carbazole, gave a yield of 78.3% of theory from tetra-chloro-anthraquinone. Nitrogen 5.01% - Chlorine 0.33%.

JLNB-4059, page 100.

Pentanthrimide Carbazole - Ponsol Khaki 2G

Fusion

666 Grams aluminum chloride, 100 grams sodium chloride dry were heated together to 185°C. and over one-half hour at 185-195°C. a mixture of 100 grams pentanthrimide and 40 grams sodium chloride dry was added. Heating was continued at 185-190°C. for 10 minutes, after which the reaction mass was poured into cold water, stirred one hour, filtered and washed acid-free.

Acid Oxidation

The above cake of crude color was suspended in five liters of water, to which 600 grams of 96% sulfuric acid had been added. To this was added 85 grams of sodium dichromate, and acid oxidation

was carried out for two hours at 85-90°C., after which time sodium dichromate was still present. The color was then filtered off and washed acid free, and given the following alkali-treatment.

Alkali-Treatment and Purification by a Vatting Procedure

The crude dyestuff, prepared as above, was suspended in four liters of water and 90 grams of sodium hydroxide, and 37 grams of sodium hydrosulfite was added at 55°C., which temperature was held 1/2 hour. The insoluble color was filtered off and washed with warm water. The cake was then again suspended in four liters of water, 100 grams of sodium hydroxide was added, and the whole heated at 95°C. for two hours. The color was filtered off while hot, washed free from alkali and made up to 720 grams paste with the assistance of leucanol. After milling, the extracted solids were 12.75%, equivalent to 91.8 grams of color or 91.8% of theory from pentanthrimide.

The overall yield from 1:4:5:8-tetra-chloro-anthraquinone was 71.9%. On preliminary test this material dyed 80/100 on skeins, and 85/100 on pads, much greener and brighter versus Ponsol Khaki 2G Standard, Lot 325. It was submitted as Preliminary Sample J-53-P-56 for evaluation, the results of which are to be found at the end of this report. JLNB-4059, page 102.

1:4:5-Trichloro-Anthraquinone

Preparation of a Highly Pure Sample

The method proposed was to nitrate a pure sample of 1-nitro-5-chloro-anthraquinone, and then replace the two nitro groups by chlorine in trichloro-benzene.

Purification of 1-Nitro-5-Chloro-Anthraquinone

200 Grams 1-nitro-5-chloro-anthraquinone was stirred overnight at room temperature in 1600 grams of 96% sulfuric acid. The insoluble 1-nitro-5-chloro-anthraquinone was filtered off and washed with 800 grams of 96% sulfuric acid. It was boiled out in hot water, filtered and washed. Recovery - 166.5 grams which is 83.2%.

Analysis - Chlorine - 12.77% - The theoretical chlorine content of 1-nitro-5-chloro-anthraquinone is 12.35%.
Nitrogen - 4.63% - The theoretical nitrogen content of 1-nitro-5-chloro-anthraquinone is 4.87%.
Melting Point - 308°C.
JLNB-4059, page 104.

## Nitration of 1-Nitro-5-Chloro-Anthraquinone

160 Grams 1-nitro-5-chloro-anthraquinone (purified) and 1000 grams 98-99% sulfuric acid were mixed and cooled to 5°C. and 42 grams of 96% nitric acid was added dropwise at 5-8°C. over one hour. The nitration mass was stirred overnight at room temperature and then heated to 40°C. for one hour, after which it was drowned in cold water. The precipitated dinitro-chloro-anthraquinone was filtered off and washed acid free. Yield - 181 grams which is 97.3% of theory.

Analysis - Chlorine - 10.97% - The theoretical amount of chlorine in dinitro-chloro-anthraquinone is 10.67%.
Nitrogen - 8.13% - The theoretical amount of nitrogen in dinitro-chloro-anthraquinone is 8.43%.
Melting Point - 322°C.
JLNB-4059, page 106.

## Chlorination of Dinitro-Chloro-Anthraquinone

178 Grams of dinitro-chloro-anthraquinone, as above prepared, was suspended in 1050 grams trichloro-benzene and heated to 200°C. at which temperature chlorine gas was passed in slowly for 14 hours. The trichloro-anthraquinone was filtered off after cooling, washed with ortho-dichloro-benzene to replace mother liquor, and the ortho-dichloro-benzene wet cake was redissolved by heating at 175°C. in 800 grams of ortho-dichloro-benzene together with five grams of charcoal. Clarification was effected by filtering hot, and the 1:4:5-trichloro-anthraquinone was allowed to crystallize by slow cooling with agitation, after which it was filtered off, and washed with ortho-dichloro-benzene and alcohol.

Analysis - Chlorine - 34.63% - The theoretical amount of chlorine in trichloro-anthraquinone is 33.97%.
Nitrogen - 0.01%
JLNB-4059, page 106.

## Tetranthrimide Carbazole - Caledon Khaki R

### Tetranthrimide

31.1 Grams 1:4:5-trichloro-anthraquinone (M.P. 264°C.), 66.9 grams α-amino-anthraquinone purified, 450.0 grams nitrobenzene, 35.0 grams soda ash, 4.0 grams copper acetate, and 0.1 grams copper powder were heated together at 200-205°C. for 8 hours. The

temperature was then lowered to 150°C., and after 8 hours the tetra-anthrimide was filtered off, washed with nitrobenzene and then steamed. Yield - 88 grams which is 100% of theory. JLNB-4059, page 110.

Tetranthrimide Carbazole

A melt consisting of 579 grams aluminum chloride and 87 grams dry sodium chloride was prepared by heating to 185°C. and at 185-190°C. a mixture of 87 grams of tetranthrimide and 35 grams of dry sodium chloride was added over 20 minutes, after which the fusion was kept at 190-195°C. for a further 10 minutes. It was cooled to 160°C. and drowned in cold water. The crude dyestuff was filtered off and washed acid-free with hot water. It was subjected to acid oxidation by suspending the cake in four liters of 8-10% sulfuric acid containing 90 grams of sodium dichromate at 90-95°C. for four hours. At the end of this period of heating, dichromate was still present. The dyestuff was filtered off, and washed acid free with hot water. It was then subjected to an alkali-vatting treatment, by suspending the cake in 4 liters of water, containing 50 grams of sodium hydroxide at 55°C. 30 Grams of sodium hydrosulfite was added and a temperature of 55°C. was maintained for 1/2 hour, after which the dyestuff was filtered off, and washed alkali free with warm water. It was made up to 600 grams of paste with the assistance of leucanol having an extracted solids of 10.28%, which is equivalent to 61.7 grams of dyestuff or 70.9% of theory.

The overall yield of dyestuff from trichloro-anthraquinone is 70.9%. After milling this product was submitted as preliminary sample J-53-P 57 for further evaluation by the Technical Laboratory. JLNB-4059, page 114.

After evaluation of the pentanthrimide carbazole (Ponsol Khaki 2G) and tetranthrimide carbazole (Caledon Khaki R) the Technical Laboratory reported as follows, the following being taken from Memo. 1100-B.

Summary

Tests have been made where the samples J-53-P-56 and J-53-P-57 were substituted for Ponsol Khaki 2G Paste, Standard, in a typical O.D. No. 7 formulation. These tests showed so very little difference in fastness that no technical advantage or disadvantages over our present standard should be stressed.

Application Properties

| | Coagulation | | |
|---|---|---|---|
| | Acid | Alkaline | Migration |
| Khaki 2G Paste, Standard | Poor | Poor | Poor |
| Khaki 2GP Paste, Standard | Moderate | Fairly good | Moderate |
| P.S.A. #21790 (I.C.I.) | Moderate to poor | Poor | Poor |
| P.S. 978, J-53-P-56 | Moderate | Fairly good | Moderate |
| P.S. 979, J-53-P-57 | Poor | Fairly good | Moderate to poor |

Shade and Strength - On Cotton Skeins - Vol. 20:1

Comparison of P.S. 978, J-53-P-56 with Ponsol Khaki 2G Paste, Standard, Lot 325.

Shade - much greener, noticeably brighter
Strength - 53:100 - 4.5 lbs. = 8.4 lbs.
Exhaust - trace superior

Comparison of P.S. 979, J-53-P-57 with Ponsol Khaki 2G Paste Standard, Lot 325:

Shade - much redder, trace duller
Strength - 95:100 - 8.0 lbs. = 8.4 lbs.
Exhaust - trace inferior

Comparison of P.S. 978, J-53-P-56 with Caledon Khaki RS Paste, P.S.A. No. 21790

Shade - much greener, considerably brighter
Strength - 35:100 - 4.5 lbs. = 11.5+ lbs.
Exhaust - noticeably superior

Comparison of P.S. 979, J-53-P-57 with Caledon Khaki RS Paste, P.S.A. No. 21790.

Shade - much greener, noticeably brighter
Strength - 63:100 - 7.2 lbs. = 11.5 lbs.
Exhaust - trace superior

Solids

P.S. 978, J-53-P-56 - 12.52% Ext. A & E
P.S. 979, J-53-P-57 - 10.08% Ext. A & E
P.S.A. No. 21790 - 11.9% Ext. A & E
Khaki 2G Paste, Standard, Lot 325 - 9.4% Ext. A & E

Fastness Properties

Comparison of the fastness properties of the samples listed below, with those of a 12.6 oz./gal. padding of Ponsol Khaki 2G Paste Standard, Lot 325.

| | 7.15 oz./gal. P.S. 978 J-53-P-56 | 11.5 Oz./Gal. P.S. 979 J-53-P-57 |
|---|---|---|
| 0.3% Chlorine | Appreciably inferior | Trace superior |
| One laundry wheel treatment | Similar | Trace superior |
| Five laundry wheel treatment | Trace superior | Trace to noticeably superior |
| Scrubbing with soap | Similar | Trace superior |
| 40 Hour Fade-Ometer exposure | Appreciably inferior | Trace to noticeably inferior |
| 20 Day weather exposure | Trace inferior | Noticeably inf. |
| 30 Day weather exposure | Trace inferior | Trace inferior |

Comparison of the fastness properties of the samples listed below with those of an 18.4 oz./gal. padding of P.S.A. No. 21790, Caledon Khaki RS Paste (I.C.I.)

| | | |
|---|---|---|
| 0.3% Chlorine | Appreciably inferior | Similar |
| One laundry wheel treatment | Similar | Trace superior |
| Five laundry wheel treatment | Similar | Trace superior |
| Scrubbing with soap | Trace inferior | Similar |
| 40 Hour Fade-Ometer exposure | Appreciably inferior | Trace inferior |
| 144 Hour Fade-Ometer exposure | Appreciably inferior | Trace inferior |
| 20 Day weather exposure | Noticeably superior | Noticeably sup. |
| 30 Day weather exposure | Noticeably superior | Similar |

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