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"LITHOSOL" FAST VIOLET 4RNL PASTE

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"LITHOSOL" FAST VIOLET 4RNL PASTE
"LITHOSOL" FAST VIOLET 4RN PASTE

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ABSTRACT

The results obtained in a series of investigations undertaken for the purpose of improving these colors in quality and yield are summarized.

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Introduction

The overall purpose of this investigation was to improve these colors in quality and yield. This report is presented in the form of an outline of the work undertaken and a summary of the findings. Recommendations, when appropriate, are made as each phase of the study is discussed.

Results

The objectives of the study were only partially attained. A number of important process improvements were made and several promising leads for future investigation were uncovered. However, the process conditions necessary for the production of "Lithosol" Fast Violet 4RN Paste consistently equal to standard in shade still remain to be established.

The following is a list of the important accomplishments of the study:

1. A process using filter cake in place of dried, ground isodibenzanthrone was developed for the chlorination step in the production of "Ponsol" Brilliant Violet 4RN Crude Wet. Savings are realized through the elimination of the drying and grinding procedures for the intermediate (see Part I, Section 4).

2. Material failing to meet standard in the solvent bleed test for "Lithosol" Fast Violet 4RNL Paste can be improved satisfactorily by rebleaching or by a purification consisting of a filtration from the reaction medium at the chlorination step (see Part I Section 7 and Part I Section 13a).

3. The optimum chlorine content of the crude color and the optimum conditions for bleaching "Lithosol" Fast Violet 4RN Paste Crude Acid were established. As the study progressed there was some evidence that the bleach conditions used for the crude color could be modified or the step eliminated entirely (see Part I Sections 11 and 13).

4. Water and iron salts as contaminants in the chlorination medium are detrimental to color quality. Water in relatively large amounts acts as a chlorination inhibitor (see Part II Sections 3a and 3h).

5. An increase in the amount of dispersant used in the regular milling during standardization of "Lithosol" Fast Violet 4RNL Paste resulted in a marked improvement in hue and brilliance of final color (see Part I Sections 10 and 19 but also note Part II Sections 4 and 6Aa).

6. "Lithosol" Fast Violet 4RNL Paste can be standardized directly from selected charges of "Ponsol" Brilliant Violet 4RN Crude Bleached. Also, color prepared from selected crudes by the viscous milling technique used in the "Lithosol" Fast Violet 4RN Paste process is satisfactory for the 4RNL type. Establishment of either one of these procedures, which would be dependent on the production of uniformly high quality crudes, would result in substantial savings through the elimination of drying, acid-pasting and bleaching steps (see Part I Sections 15, 16, 22 and 24).

7. A statistical study indicated a serious lack of reproducibility in the testing procedure used for evaluation of "Lithosol" Fast Violet 4RNL Paste quality (see Part I Sections 17 and 23).

8. A viscous milling procedure resulting in improved quality and considerable savings was developed for "Lithosol" Fast Violet 4RN Paste (see Part II Section 4).

9. Impairment of color quality of "Lithosol" Fast Violet 4RN Paste, as indicated by a shift in shade from red to blue in paper dyeings may occur with certain physical treatments including very prolonged viscous milling and acid pasting (see Part II Section 6A). In work of a preliminary nature a digestion procedure was developed which reversed this shift in shade. Correlations were shown between shade on paper and the appearance of diffraction rings produced in electron microscope studies of the color (see Part II Section 6B).

PART I

"LITHOSOL" FAST VIOLET 4RNL PASTE

Introduction

This color is marketed for the pigment trade and is used in paints, varnishes and enamels. Late in 1956 it was reported that material then being produced was unsatisfactory because of weakness and dullness in lithovarnish rub-out testing. At this time the color was made according to the following procedures:

1. Suspending dry isodibenzanthrone in o-dichlorobenzene and chlorinating to the dichloro derivative with sulfuryl chloride in the presence of iodine as a catalyst.

2. Removing the reaction solvent by steam distillation and isolating the crude color from the steam still slurry by filtration.

3. Purifying the crude color by bleaching with hypochlorite.

4. Effecting a further purification by acid-pasting the dried crude and bleaching again with hypochlorite.

Some time prior to this period a change was made in the procedure for the preparation of isodibenzanthrone. This consisted of the substitution of methyl alcohol for ethyl alcohol in the alcoholic potassium hydroxide fusion melt and was made for reasons of economy and convenience (Ref. No. 1).

See Appendix 1 for an outline of the steps involved in the current production of this color starting with benzanthrone.

Experimental

To correct the above mentioned deficiencies in the final color and generally to improve the processes involved, the following studies were undertaken:

1. Reevaluation of methyl alcohol as a substitute for ethyl alcohol in the process for isodibenzanthrone crude.

2. Purification of the isodibenzanthrone crude by vatting.

3. Purification of the isodibenzanthrone crude by acid crystallization.

4. Rebleaching and improving the crude color bleaching procedure.

5. Using anionic, cationic and nonionic surfactants in the acid-pasting drowning water.

6. Evaluation of variations in the chlorine content of the crude color.

7. Using the isodibenzanthrone as filter cake and dehydrating the o-dichlorobenzene suspension prior to chlorination.

While these studies were in progress a new analytical procedure, consisting of a spectrophotometric analysis, was developed for isodibenzanthrone (Orchem Method 52-5-11-1). With it isodibenzanthrone content (purity) and dibenzanthrone as the principal impurity can be determined. Although this procedure is an improvement over the older method (acid pasting recovery) it can account for only 70 to 80% of the material present and is thus of questionable merit as a research tool.

The results obtained in these studies are summarized as follows:

1. Replacement of methyl alcohol with ethyl alcohol in the fusion melt resulted in some instances in improved isodibenzanthrone and in final color. Although the findings were not conclusive the ethyl alcohol procedure was reestablished as standard practice (Ref. No. 2).

It is recommended that the return to the use of methyl alcohol be considered, particularly if an improved analytical method for isodibenzanthrone is developed.

2. Isodibenzanthrone purified by yatting tended to give improved color by lithovarnish rub-out testing (CWNB 1696 pages 30-33). Plant trial runs demonstrated that this procedure is operable and that the reslurry and oxidation steps are unnecessary (Ref. No. 3). However, these changes were not adopted because of inconclusive results in the final color testing.

3. Isodibenzanthrone, purified by crystallization from sulfuric acid, failed to give improved color. Filtration difficulties were experienced especially when the acidity was adjusted to strengths much below 93.0%. At acidities higher than 93.0%, the yield loss was excessive (CWNB 1696 pages 18-21, 24-29, 34-36, 39-40, 47-51).

4. It was demonstrated that in the chlorination step the isodibenzanthrone can be charged as filter cake instead of being first dried and ground. The cake is suspended in the reaction medium and dehydrated before chlorination. This change was adopted as standard practice (Ref. No. 4).

5. In some laboratory runs it was shown that bleaching of the crude color could be eliminated (CWNB 1696 pages 99-113). Because of testing uncertainties this change was not given a plant trial. This point should be investigated further.

6. The use of cationic, anionic and nonionic surfactants in the acid-pasting drowning water had no effect on color quality (CWNB 1655 page 178).

The conclusions drawn from the above phase of the investigation were based on lithovarnish rub-out testing which was subsequently proved to be unreliable.

Although certain process fundamentals had been established at this point, lack of uniformity in final color quality persisted. The investigation was continued as follows:

Solvent Bleed

7. In August, 1957 it was reported that several lots failed to meet the solvent bleed specification. This test had been suspended for several years but was reinstated at a customer's request. It was shown that the solvent bleed deficiency could be corrected by rebleaching the color. This treatment also improved shade in the lithovarnish rub-out test and in a newly established jiffy paint grind testing procedure (CWNB 1738 pages 54-55, 100-101). This method of improving the color was demonstrated again early in 1958 (CWNB 1814 pages 15-16, 102-103, 129-131, 178-179).

Acid Pasting

8. At this time a study was started to determine the optimum acid-pasting conditions for the production of uniformly satisfactory color. Many sets of conditions were tried and a number of additives were used in the drowning water. The results, based on lithovarnish rub-out and jiffy paint grind testing, were inconclusive (CWNB 1738 pages 137-138, 148-149, 151-152, 157, 159-164, 177-178; CWNB 1765 pages 194-195; CWNB 1814 pages 3, 8, 17-19, 23-25, 59-62, 77-81, 93-96).

o-Dichlorobenzene vs. Nitrobenzene as the Chlorinating Medium

9. In the chlorination step, nitrobenzene would be preferred to o-dichlorobenzene as the reaction medium because of occasional difficulties with the control chlorine analysis due to incomplete removal of the solvent. In addition, nitrobenzene is the cheaper solvent. In an evaluation study it was shown that with nitrobenzene the color quality was not significantly different from the control, using o-dichlorobenzene. This was true for both vatted and unvatted isodibenzanthrone. It was concluded, therefore, that although there are certain advantages for nitrobenzene they are outweighed by the hazardous nature of this material and that o-dichlorobenzene should be retained as the chlorinating medium (CWNB 1765 pages 168-169, 171-172, 194-195). (See also Part II, Experimental Section No. 3k.)

Milling with a Manton-Gaulin Mill vs. HF Milling

10. In a milling study it was shown that material testing blue and dull by the lithovarnish rub-out procedure after passage through a Manton-Gaulin mill will be red and bright after HF milling. The redness is accentuated when the amount of dispersant, Compound 8, is doubled (CWNB 1814 pages 26-27).

Optimum Chlorine Content of Crude Color

11. In a study in which unvatted isodibenzanthrone was under- and overchlorinated, it was shown that the optimum final chlorine content of the color lies between 14.0 and 15.0% (the theoretical value for the dichloro derivative is 13.5%). Overchlorination tends to give darker masstones, redder shades and heavier solvent bleeds; underchlorination gives bluer shades. It was observed that the chlorine content will drop as much as one percentage point during the bleaching and acid-pasting procedures. It is, therefore, necessary to use 14.5 to 15.5% as the control chlorine specification (CWNB 1814 pages 44-47). This value has been established as standard practice (Ref. No. 5).

Vatted vs. Unvatted Isodibenzanthrone

12. Samples of vatted and unvatted isodibenzanthrone were converted to color by the regular processes of chlorination, steam distillation, acid-pasting and bleaching. It was concluded from the results obtained in lithovarnish rub-out testing that vatting is not necessary (CWNB 1814 pages 52-58).

Bleaching Studies

13(a). A composite of isodibenzanthrone charges was chlorinated by the regular procedure to the crude color. This was filtered from the solvent and washed with fresh solvent as a means of purification and then steam-distilled. One portion of the purified color was acid-pasted and bleached; another portion was bleached first and then acid-pasted. All final colors were very good in lithovarnish rub-out and solvent bleed testing and in the jiffy paint grind test. The procedure of acid-pasting first and then bleaching gave slightly better results. "Lithosol" Fast Violet 4RNL is now made by acid-pasting crude and then bleaching (Ref. No. 6). It should be noted that the crude color was

not given the usual bleach treatment, which suggests that this step could be omitted if the color is to be produced as "Lithosol" Fast Violet 4RNL Paste. However, the laboratory crude was solvent-filtered, whereas the plant crude is not.

This study also showed that the purification by filtration from the solvent is an excellent means of obtaining a color which will satisfy the solvent bleed specification (CWNB 1814 pages 20-22, 112-119, 172-176).

13(b). In a later study, involving the paste crude color, it was shown that one-quarter to one-half part of bleach is the optimum. In this case the color had already received the regular bleach treatment at the crude stage. The hypochlorite (outside) bleach has slightly less dulling effect than chloride (inside) bleach (CWNB 1932 pages 33-34, 70-80). Principally because of convenience, one-half part of inside bleach has been established as standard practice (Ref. No. 6).

Salvage of Off-quality Material

14. Lots 86 and 88 of "Lithosol" Fast Violet 4RNL Paste were extremely blue in lithovarnish rub-out and in jiffy paint grind testing. Laboratory runs indicated that this could be corrected by an alkali-boil treatment (CWNB 1876 pages 187-189; CWNB 1910 page 25). Lot 86 was upgraded satisfactorily by this procedure; Lot 88 failed to respond and had to be disposed of as the "Ponsol" type for the textile trade (Ref. Nos. 7 and 8).

Elimination of the Paste Crude Acid Pasting and Bleaching Steps

15. Lots 90 and 92 of "Lithosol" Fast Violet 4RNL Paste were made by milling directly "Ponsol" Brilliant Violet 4RN Crude Bleached, thus eliminating the usual acid-pasting and final bleaching steps (CWNB 1910 pages 124-125). Lot 90 was satisfactory in lithovarnish rub-out testing; Lot 92 was not. The shortened procedure, therefore, had to be abandoned pending further investigation. It has attractive possibilities.

Conversion of "Lithosol" Fast Violet 4RN to "Lithosol" Fast Violet 4RNL

16. The redness, brightness and strength brought out in the viscous milling procedure used in the "Lithosol" Fast Violet 4RN Paste process can be retained for "Lithosol" Fast Violet 4RNL Paste. The large amount of dispersant present in the 4RN type is first destroyed by an acid boil, the color isolated by filtration and then redispersed by the normal procedure for the 4RNL type (CWNB 1910 pages 43, 60-62, 80).

It might be possible to destroy the excess dispersing agent with bleach and then standardize as the 4RNL type. It is recommended that this procedure be tried.

TF 10-24 Testing Procedure

17. At this point in the investigation, a new procedure for evaluating final color was established. It was the Pigments Department's full paint grind test designated as TF 10-24. It replaced the lithovarnish rub-out and the jiffy paint grind procedures, both of which were found to be unreliable. It was learned later that the new test was also unreliable, possibly because the method details differed significantly from the procedure used at Pigments Department (see Section 23 of this study).

Effect of Triton X-100

18. Using the TF 10-24 testing procedure it was shown that the addition of 1 to 3% Triton X-100, a nonionic dispersing agent, would bring out redness and brightness in color previously judged blue and dull (CWNB 1910 pages 162-163, 167, 172; CWNB 1932 pages 107-108). However, the use of this additive was prohibited by the Pigments Department (Ref. No. 9).

Increase in Dispersant

19. A fourfold increase in the amount of Compound 8 used as the dispersant resulted in marked improvement in redness and brightness of final color (CWNB 1918 page 153).

Lot 94 of "Lithosol" Fast Violet 4RNL Paste was prepared with this change in procedure and was judged satisfactory in TF 10-24 testing. This demonstrated that the additional amount of dispersing agent is necessary and can be tolerated in the final paste. This change has been adopted as standard practice (Ref. No. 10)(see also Part II Section 4).

Additional Studies

20(a). In a renewal of the acid-pasting study by other workers (C. E. Carr and F. C. Eberly) many variations in the technique were tried. The results were generally inconclusive. Samples testing satisfactorily in the lithovarnish rub-out procedure were generally unsatisfactory in the TF 10-24 paint grind testing. Some of the acid-pasting conditions led to material which jelled in the paint grind system (CWNB 1918 pages 112, 115, 118, 130-132, 134, 140-141, 159, 166-170, 172-173, 182-183, 185-189; CWNB 1905 pages 61-63, 65, 68, 76, 78, 87-88, 95).

20(b). Color made from crudes extracted with boiling acetic acid and crudes prepared from purified isodibenzanthrone (solvent-extracted and acid-crystallized) gave unsatisfactory results in TF 10-24 testing (CWNB 1932 pages 25-27; CWNB 1918 pages 108, 114, 116, 120-121, 124, 130-131, 135, 137, 139, 142-143, 149, 157, 161, 163).

20(c). Vatting of the crude color followed by oxidation and bleaching was not beneficial (CWNB 1918 pages 147, 172-173).

20(d). Milling with a dispersant after acid-pasting and before bleaching brightened the color (CWNB 1932 pages 72-73, 76-78). This change in process has not been given a plant trial.

Quality of Competitive Products

21. In May, 1959, seven competitive products were tested against our standard using the TF 10-24 procedure. The results are listed in the following table (Ref. No. 11):

Parts	Material	Shade
100	"Lithosol" Fast Violet 4RNL Paste Lot 83	Standard
105	Cibanone Violet 4R Double Paste	2 Blue, 2 dull
100	Calcosol Violet 4RP Single Paste	1 Blue, 3 dull
102.5	Indanthrene Brilliant Violet 4R Infra Paste	3 Blue, 1 dull
100	Sandothrene Violet N4R Double Paste	1 Blue, 2 dull
110	Sandothrene Printing Violet N4R Double Paste	4 Red, 1 dull
-	Carbanthrene Brilliant Violet 4R Paste	Jelled
975	Calcoloid Violet 4RD Single Paste	2 Blue

These results show that these competitive products do not approach the "Lithosol" offering in shade and brilliance.

Elimination of the Acid-Pasting and Final Bleaching Steps

22. Earlier in the study (Section 16) it was pointed out that the redness, brightness and strength brought out in the viscous milling in the "Lithosol" Fast Violet 4RN Paste procedure will be retained after the dispersant is destroyed by an acid boil and the color redispersed. It was later shown that many laboratory samples and plant charges made by the regular viscous milling of "Ponsol" Brilliant Violet 4RN Crude Bleached were excellent in TF 10-24 and Fade-Ometer lightfastness testing and entirely satisfactory as "Lithosol" Fast Violet 4RNL Paste (CWNB 1932 pages 81-82, 163, 174-176; CWNB 1949 pages 4-5, 23, 25, 93, 102) (see also Part II, Section 4).

This change should be considered for plant adoption because of the considerable savings possible through the elimination of the drying, acid-pasting and bleaching steps now normal for this color.

Reproducibility of the
TF 10-24 Testing Procedure

23. The testing inconsistencies experienced with the lithovarnish rub-out and jiffy paint grind procedures seemed to continue after the establishment of the Pigments Department's full paint grind test, TF 10-24. To verify this observation, the following statistical study of the method was carried out:

Six samples from each of six different lots, including the standard lot, were prepared and coded for testing. Half of these samples were laked at the "Ponsol" Laboratory by two individuals; the remainder were laked at Technical Laboratory. All laked samples were tested at Technical Laboratory by the TF 10-24 procedure set up by this group. This testing included both the 50:50 and the 5:95 tintings with a white base.

The statistical findings proved that significant shade and strength discrimination existed among the testing personnel and indicated serious lack of reproducibility in the TF 10-24 testing procedure (Ref. No. 12). It was recommended that the necessary adjustments to the procedure be made and the statistical study be repeated.

"Lithosol" Fast Violet
4RN Double Paste

24. In response to a request by the Pigments Department for a cheaper color in the form of a double paste, Lot 1 of "Lithosol" Fast Violet 4RNL Double Paste was prepared from selected charges of "Ponsol" Brilliant Violet 4RN Crude Bleached which were O.K. for paper dyeing. The press cakes were put through a Follows and Bate mill in the presence of the normal amount of dispersing agent and a small amount of carboxymethyl cellulose added as a thickener. The lot was entirely satisfactory in TF 10-24 and solvent bleed testing against the standard Lot 83 of "Lithosol" Fast Violet 4RNL Paste and was produced at an estimated savings of 80¢/pound (Ref. Nos. 13 and 14).

The shortened procedure was similar to that used for Lot 90 of regular production, reported in Section 15 of this study.

It is recommended that more consideration be given to this method of producing the 4RNL type. It will be necessary to use selected charges of "Ponsol" Brilliant Violet 4RN Crude Bleached until process controls are developed and applied so that uniform high-quality material is produced at the crude stage. This phase of the overall problem is discussed in Part II of this report.

PART II

"LITHOSOL" FAST VIOLET 4RN PASTE

Introduction

This color is marketed as a pigment and is used to dye paper. For many years quality has been inconsistent from lot to lot principally because of uncontrollable shade differences. A study to correct this deficiency has been carried out simultaneously with that reported in Part I for the 4RNL type.

Many of the changes studied in Part I were evaluated by standard paper dyeings but were generally ineffective in producing a color of uniform quality.

See Appendix 1 for an outline of the steps involved in the current production of this color starting with benzanthrone.

Experimental

The following additional studies for product and process improvements were undertaken:

1. Acid-Pasting

The following acid-pasting procedures were tried. None was successful in producing uniformly satisfactory color. In general, shades were much too blue compared with standard.

(a) Use of 101.5% sulfuric acid to dissolve the crude color (CWNB 1696 pages 167-169).

(b) Turbulent drowning (CWNB 1696 pages 199-200).

(c) Acid swelling - slurry in 85% sulfuric acid (CWNB 1738 pages 13-14, 45-47).

(d) Use of Glauber's Salt in the acid (CWNB 1738 pages 15-16, 45-47, 151-152).

(e) Drown to 36% acidity (CWNB 1738 pages 17, 45-47).

(f) Drip-drown in ice and water (CWNB 1738 pages 47, 148-149).

(g) Drown in boiling sodium hydroxide solution (CWNB 1738 pages 50-51, 151-152).

(h) Drip-drown in boiling water (CWNB 1738 pages 50-51).

(i) Drown in boiling saturated sodium sulfate solution (CWNB 1738 pages 65-66, 149).

(j) Drip-drown in a boiling solution of sodium hydroxide and sodium hypochlorite (CWNB 1738 pages 65-66, 151-152).

(k) Drip-drown in boiling water then bleach with sulfur dioxide (CWNB 1738 page 76).

(l) Drip-drown in different amounts of boiling water (CWNB 1738 pages 144-145).

(m) Drip-drown in water at 85 to 90°C. containing "Alkanol" HC (CWNB 1738 pages 148-149).

(n) Use of naphthalene in the acid (CWNB 1738 pages 148-149).

(o) Drip-drown in a boiling solution of sodium carbonate (CWNB 1738 pages 151-152).

(p) Drip-drown at 20 to 40°C. using a special funnel (CWNB 1738 pages 159-160).

(q) Drip-drown at 20 to 40°C. and at 85 to 90°C. with a special funnel and using nitrobenzene in the acid (CWNB 1738 pages 159-160).

2. Vatting

The following vatting procedures were tried. None was successful and again the color shades were much too blue compared with standard.

(a) Vatting during HF milling with the milling continued after the vat was destroyed by slow oxidation (CWNB 1738 pages 62, 68-69).

(b) Passage through a Manton-Gaulin mill in the presence of triethanolamine, then vatting and oxidation with "Sitol" oxidizing agent and the milling continued (CWNB 1738 pages 63-64).

(c) Vatting, oxidizing and bleaching (CWNB 1738 page 158).

3. Chlorination

Because it is possible that the cause for persistent blue shades is at least partly chemical, the chlorination step to produce the crude color was investigated as follows:

(a) Water as a Contaminant

One factor suspected of adversely affecting the reaction is the presence of a small amount of water. Sulfuryl chloride, the chlorinating agent, will react with water to form sulfuric acid and hydrochloric acid. The former might direct the chlorine into undesirable isomer positions in the isodibenzanthrone molecule. Such by-product formation could be responsible for blue shades of final color. Water could be present because of the incomplete dehydration of the o-dichlorobenzene-isodibenzanthrone slurry.

In one run the slurry was dehydrated thoroughly and then contaminated with 2% water prior to chlorination. Gross underchlorination (6% vs. the standard of 14 to 15% chlorine) resulted even after repeated additions of sulfuryl chloride (CWNB 1970 pages 94-96).

For a smaller amount of water (0.4%) chlorination was complete but the final color was judged 3 blue 4 dull against standard; a control was judged 3 blue, 4 bright against standard (CWNB 1970 pages 155-158).

These results indicate that water is detrimental and in relatively large amounts will act as a reaction inhibitor.

It is recommended that this factor be studied further and that plant equipment be inspected frequently for sources of water.

(b) Sulfuric Acid as a Contaminant

Thoroughly dehydrated o-dichlorobenzene-isodibenzanthrone slurry was contaminated with 6% of 98% sulfuric acid just prior to chlorination. Even with double the process amount of sulfuryl chloride and an extended reaction period, the chlorination was negligible (1.2% chlorine)(CWNB 1970 page 120).

This result indicates that under the conditions imposed, sulfuric acid in the amount used will inhibit the reaction.

(c) Hydrochloric Acid as a Scavenger

Because of incomplete filter cake washing the isodibenzanthrone often contains sodium hydroxide as a contaminant. The alkali will react with sulfuryl chloride with the reaction products possibly acting as inhibitors. Prior to dehydration, a reaction slurry which tested strongly alkaline was acidified with hydrochloric acid, dehydrated and then chlorinated according to process conditions.

The results were inconclusive. No improvement over a control sample was realized; both samples were bluer than standard (CWNB 1970 pages 140-143).

(d) Thionyl Chloride as a Scavenger

Thionyl chloride reacts with water to form hydrogen chloride and sulfur dioxide and, unlike sulfuryl chloride, leaves no sulfuric acid residue. It should, therefore, serve as a water scavenger.

Thoroughly dehydrated reaction slurry was contaminated with 0.4% water. Sufficient thionyl chloride to destroy the water was added and the chlorination carried out according to process.

The results were inconclusive. No improvement over a control sample was realized; both samples and the control were judged 3 blue against standard (CWNB 1970 pages 140-143). The procedure was given a plant trial with inconclusive results (Ref. No. 15).

It is recommended that the use of thionyl chloride as a water scavenger be considered seriously for inclusion in the regular procedure as a precautionary measure.

(e) Effect of alpha-Picoline

alpha-Picoline appears occasionally as a contaminant in the plant recovered o-dichlorobenzene. Addition of 3.0% of this material to fresh o-dichlorobenzene used in the regular chlorination had no detrimental effect on final color (CWNB 1970 pages 140-143).

(f) Fresh vs. Recovered o-Dichlorobenzene

Regular chlorinations were run in fresh and recovered o-dichlorobenzene. Slightly better color was obtained when the former was used, indicating the possibility of miscellaneous detrimental contaminants in the recovered o-dichlorobenzene (CWNB 1970 pages 152-152; CWNB 1994 pages 6-8).

(g) Monochlorobenzene as the Reaction Medium

Inferior color was obtained when monochlorobenzene was used in place of o-dichlorobenzene as the chlorination medium (CWNB 1970 pages 152-154).

(h) Effect of Iron

During the chlorination, contamination with iron salts could occur from the action of sulfuryl chloride vapors and hydrochloric acid on the upper parts of the reaction system. To determine whether such contamination is detrimental, a run was made using o-dichlorobenzene containing 0.7% ferrous chloride ($FeCl_2 \cdot 4H_2O$). Final color was inferior in shade to a control sample indicating that kettle corrosion is a definite factor in product eterioration and must be avoided (CWNB 1970 pages 155-158).

It is recommended that the chlorination equipment be inspected at intervals to eliminate any possible sources of iron contamination.

(i) Catalysts

The regular chlorination catalyst is iodine. The substitution of potassium iodide for iodine resulted in no

improvement in color quality. In this study it was shown that satisfactory chlorination can be accomplished without a catalyst particularly when a high reaction temperature (100 to 105°C. vs. the process temperature of 65 to 70°C.) is used (CWNB 1994 pages 96-98, 112-113).

Indifferent results were obtained in plant trial runs using potassium iodide as the catalyst (Ref. No. 16).

It is recommended that higher temperature non-catalytic chlorinations be tried in plant runs.

(j) Chlorination with Thionyl Chloride

An unsuccessful attempt was made to chlorinate with thionyl chloride in place of sulfuryl chloride. The reaction was carried out at reflux (125 to 130°C.) over a period of six hours. The chlorine content of the product was only 11.6% as compared with the control level of 15 to 16%. A final sample for dyetesting was not prepared (CWNB 1994 page 114).

As thionyl chloride is an excellent water scavenger, it is recommended that this investigation be continued.

(k) Nitrobenzene vs. o-Dichlorobenzene as the Chlorinating Medium

The following table summarizes the results obtained in a study to compare nitrobenzene with o-dichlorobenzene as the chlorinating medium using vatted and unvatted isodibenzanthrone. Regular chlorination and bleaching procedures were used and the final samples were prepared by the viscous milling technique (CWNB 1765 pages 168-169, 171-172, 186-193)(see also Part I, Experimental Section No. 4).

Type of Isodi-benzanthrone	Reaction Medium	Paper Dyeing vs. Standard	
Vatted	o-Dichlorobenzene	2-1 Blue, 2-1 bright	+20
Vatted	Nitrobenzene	Off-shade, brighter	-10
Unvatted	o-Dichlorobenzene	3 Blue, 3 bright	-10
Unvatted	Nitrobenzene	2 Blue	-10

These results indicate that o-dichlorobenzene is the preferred reaction medium and that purification of the isodibenzanthrone by vatting is not necessary and is actually somewhat detrimental.

(1) Isodibenzanthrone Quality

To demonstrate that the quality of the final color is dependent to some degree on the quality of the starting isodibenzanthrone, two selected charges were chlorinated. The regular chlorination and bleaching procedures were used and the final color paste prepared by the viscous-milling technique. In addition, the chlorination mass was filtered and the cake washed with fresh solvent (CWNB 1910 pages 141-143).

The results are summarized in the following table:

Isodibenzanthrone				
Charge No.	Purity	Dibenz.	Paper Dyeing vs. Standard	
86	83.3%	7.0%	5-4 Bright	-10
87	75.3	4.5	1 Blue	+20

These results indicate that in this study superior color was made from the better quality isodibenzanthrone.

It is recommended that an improved procedure for determining isodibenzanthrone quality be developed by the Analytical Methods Improvement Group and a satisfactory Quality Control Limit be established.

4. Viscous Milling

A study showed that substantial improvements, particularly in intensity and brilliance, result when the final paste is prepared by viscous-milling the bleached crude color (CWNB 1696 pages 170-171, 178-183, 194-195, 197-198; CWNB 1738 pages 23-24, 75, 77).

Four plant trial charges of "Ponsol" Brilliant Violet 4RN Crude Bleached VM were made by this technique (Ref. No. 17). This material was standardized to three lots of "Lithosol" Fast Violet 4RN Paste with an average solids content of 7.7% as compared with the standard solids of 11.7%. This procedure resulted in a 20% reduction in mill cost which, on the basis of an annual production of 60,000 lb., represented a gross annual savings of approximately $17,000.

Because of this excellent performance, the viscous milling procedure was established as standard practice (Ref. No. 18).

In the plant procedure as first established, the dispersant consisted of 0.28 part of Blancol (based on the 100% weight of the crude color). A study showed that this amount usually could be reduced drastically without impairing quality or yield. The laboratory millings were done with the process amount of sand (5 to 6 parts per part of crude color) with a 3-hour milling period after attaining maximum viscosity.

The results obtained are summarized in the following table (CWNB 1932 pages 174-176; CWNB 1949 pages 4-5, 23).

Parts of Blancol	Particle Size Index	Paper Dyeing vs. Standard		
0.33	13.5		4-3 Bright	1:1
0.17	15.6		4-3 Bright	1:1
0.11	15.5	4 Red		-10
0.08	15.0		4 Bright	+15
0.06	16.9	4 Red		-10
0.03	17.1	2 Red	4 Bright	+5

As a result of this study successful plant trial runs were made using 0.075 part of Blancol. The use of 0.075-0.15 part of Blancol was recommended for adoption as standard practice (Ref. No. 19).

One reason for reducing the amount of dispersant to a minimum is the possibility of using the viscous milling technique for the production of the 4RNL type. As pointed out in Part I, Section 22, "Lithosol" Fast Violet 4RNL Paste made by this procedure is satisfactory in TF 10-24 and lightfastness testing (CWNB 1932 pages 81-82, 163, 174-176; CWNB 1949 pages 4-5, 23, 25, 93, 102)(see also Part I, Sections 16 and 19).

5. Effect of Milling Temperature

In a short study to determine the effect of milling temperature on color shade, a slight advantage was shown for 70 to 80°C. over 30 to 40°C. Two-hour viscous millings using 0.15 part of Blancol were made. A summary of the results obtained is given in the following table (CWNB 1994 page 86):

Milling Temperature	Particle Size Index	Paper Dyeing vs. Standard		
30-40°C.	12.6	4 Blue	4 Bright	-10
70-80°C.	12.4	4 Red	4 Bright	-20

6. Physical Factors Affecting Shade

The attainment of standard shade for pigment colors is dependent, in part at least, on such factors as crystal form, particle size, particle distribution and optical phenomena involving light reflection, refraction, diffusion and scattering.

In the case of the subject color, persistent blueness against standard has been the principal cause for rejection. Color on the red side of standard is acceptable. Therefore, avoidance of physical treatment which would cause a shift from red to blue is necessary and application of physical treatment which would accomplish the reverse is desirable.

A. Degradation of Color Quality

In the following study, certain physical manipulations which will degrade the color were demonstrated.

(a) Prolonged Viscous Milling

A composite of four plant charges of "Ponsol" Brilliant Violet 4RN Crude Bleached was selected for a series of laboratory millings. Plant milling of this material produced "Lithosol" Fast Violet 4RN Paste testing 3 red, 4 bright -20 against standard.

Each laboratory milling consisted of 60 g. 100% of crude color, 20 g. 100% of Compound 8 and 325 g. of fine sand. Milling periods were from 30 minutes to 16 hours after maximum viscosity was reached (CWNB 1910 pages 58-59).

The results obtained are summarized in the following table:

Milling Period, Hours	Particle Size Index	Paper Dyeing vs. Standard		
1/2	17.6	2 Red	4 Bright	-15
1	17.0	2 Red	4 Bright	-10
2	19.9	3 Red	4 Bright	1:1
4	10.7	3 Red	4/3 Bright	-5
8	13.0	4 Blue	4/3 Bright	-10
16	12.2	2 Blue	4 Bright	1:1
16	14.1	4 Blue	4/3 Bright	-5*

*Used 54 g. 100% Compound 8.

These data indicate a definite shift from red to blue as milling is prolonged.

In a 16-hour milling using a large excess of Compound 8 (54 g. 100% vs. 20 g.), the color was judged 4 blue 4/3 bright -5 against standard, showing that an increase in dispersing agent will tend to prevent the shift in shade.

Although these data also show that there is no correlation between color shade and particle size index, considerable plant experience does seem to indicate that there is such a correlation.

In a similar study using a coarser sand (Keystone Sand No. 22) prolonged milling failed to bring about a shade shift (CWNB 1910 pages 122-123).

The results obtained are summarized in the following table:

Milling Period, Hours	Particle Size Index	Paper Dyeing vs. Standard
1	19.1	3 Red +20
2	18.2	3 Red +20
4	17.1	3 Red +25
6	17.0	3 Red -30
8	16.2	3 Red -30

This type of sand was recommended for plant trials, but because of filtration difficulties with it when milling other colors, it was decided to cancel the study. In view of added experience with this technique it is suggested that this decision be reconsidered.

Using the coarser sand, a laboratory evaluation milling procedure using 20 g. 100% of crude color instead of 60 g. was developed. This procedure is useful when small samples only are available for testing (CWNB 1910 pages 151-152).

(b) Acid Pasting

Portions of plant Charge 4-6 of "Ponsol" Brilliant Violet 4RN Crude Bleached were:

1. Viscous-milled for control.
2. Acid-pasted, drip-drowned in ice and water and viscous-milled.
3. Acid-pasted, drip-drowned in boiling water and viscous-milled (CWNB 2207 pages 41-42, 67-68).

The results obtained are summarized in the following table:

Conditions	Particle Size Index	Paper Dyeing vs. Standard
Control	11.5	3 Red 4 Bright
Acid-paste (cold)	17.7	1 Blue Off-shade
Acid paste (hot)	19.5	1 Blue Off-shade

These data indicate that acid-pasting is detrimental by causing a definite shift in shade from red to blue.

(c) Vatting

A portion of plant Charge 3-525 of "Ponsol" Brilliant Violet 4RN Crude Bleached was viscous-milled for control. Another portion was vatted, oxidized by blowing with air and viscous-milled (CWNB 1994 pages 87-88, 148-149).

The results obtained are shown in the following table:

Conditions	Particle Size Index	Paper Dyeing vs. Standard
Control	17.6	4 Red 4 Bright -20
Vatted	33.7	1 Blue 4/3 Dull 1:1

These data indicate that vatting is detrimental by causing a definite shift in shade from red to blue.

(d) Solvent Digestion

Portions of plant Charges 3-523 and 3-525 of "Ponsol" Brilliant Violet 4RN Crude Bleached were viscous-milled for controls. Other portions were dehydrated in o-dichlorobenzene and held at 140 to 145°C. for six hours. The solvent was removed by steam distillation and also by filtration and washing with alcohol. All filter cakes were then viscous-milled (CWNB 1994 pages 83-84, 87-89, 109, 148-149).

The results obtained are shown in the following table:

Crude Color	Treatment	Particle Size Index	Paper Dyeing vs. Standard		
Chg. 3-523	Control	13.8	4 Red	4 Bright	-20
3-523	ODCB digest Steam distillation	16.4	1 Blue	4 Bright	+25
Chg. 3-525	Control	17.6	4 Red	4 Bright	-20
3-525	ODCB digest Steam distillation	14.8	1 Blue		1:1
3-525	ODCB digest Filtration Alcohol wash	13.9	1 Blue	4 Bright	1:1

These data indicate that prolonged digestion in o-dichlorobenzene is detrimental by causing a definite shift in shade from red to blue.

B. Upgrading of Off-quality Color

The above results indicate that degradation of the color to unacceptable blue shade can be readily accomplished by a number of procedures involving physical change. A procedure which would bring about a reversal of this effect is desirable. The following study, which is only preliminary in nature, shows that this may be possible.

Portions of plant Charge 4-6 of "Ponsol" Brilliant Violet 4RN Crude Bleached were:

1. Viscous-milled for control.
2. Acid-pasted and drip-drowned in boiling water.

A part of the acid-pasted color was suspended in a 50% solution of o-dichlorobenzene in ethyl alcohol and digested at 60 to 70°C. for 16 hours. After isolation by filtration and washing with alcohol the cake was viscous-milled by the regular procedure (CWNB 2207 pages 41-42, 67-68).

The results obtained are summarized in the following table:

Treatment	Particle Size Index	Paper Dyeing vs. Standard	
Control	11.5	3 Red 4 Bright	+25
Acid-pasting	19.5	1 Blue Off-shade 3 Bright	+20
Alcohol-ODCB digestion of acid-pasted color	13.7	3 Yellow 3 Bright	-10

Although the shade of the digested sample was judged yellow, it was more red than blue and indicated that a definite shift in the desired direction had taken place. This was the first time that red color had been degraded to blue and then restored to red.

An attempt to apply this technique to color originally on the blue side of standard was unsuccessful (CWNB 2207 page 66).

That some physical change takes place during the digestion procedure is shown by the appearance of diffraction rings produced in electron microscope studies. Material testing red on paper produces sharply defined rings; that testing blue on paper produces a diffused pattern.

It is strongly recommended that this lead be exploited. If the proper physical treatment of the final color can be established, then process alterations and improvements starting with the production of dibenzanthronyl sulfide can be studied with the assurance that the results will not be jeopardized by a last minute change which will degrade the color.

REFERENCES

1. Experimental Change in Process S.N. 56-62 for Isodibenzanthrone Crude S, dated February 29, 1956 and the corresponding Results Sheet, approved May 2, 1956.

2. Chambers Works Process for the Manufacture of Isodibenzanthrone Crude S Wet, dated August 2, 1960.

3. Test Authorizations TA-C-57-152 dated April 4, 1957 and TA-C-57-152, Part II, dated May 29, 1957 and the corresponding Test Conclusion, dated November 10, 1959.

4. Test Authorization TA-C-57-261 dated May 31, 1957 and the corresponding Test Conclusion, dated August 29, 1958.

5. Chambers Works Technical Standard 770-638 520 dated October 27, 1959, "Ponsol" Brilliant Violet 4RN Crude Wet.

6. Chambers Works Technical Standard 770-455 940, "Lithosol" Fast Violet 4RN Paste Crude Acid, dated March 28, 1960. Chambers Works Technical Standard 770-455 920, "Lithosol" Fast Violet 4RN Paste Crude, dated January 29, 1960.

7. Test Authorization TA-C-58-509 dated July 2, 1958 and the corresponding Test Conclusion, dated June 8, 1959.

8. Test Authorization TA-C-58-969 dated December 12, 1959 and the corresponding Test Conclusion, dated November 6, 1959.

9. Letter dated May 7, 1959 from Mr. H. Arnoul, Pigments Department, Newark, N.J. to Mr. R. L. Burnett, Orchem, Wilmington, Del.

10. Test Authorization TA-C-59-491 dated June 8, 1959 and the corresponding Test Conclusion, dated August 5, 1959.

11. Letter dated May 28, 1959 from T. G. Webber, Technical Laboratory to Mr. R. B. Morton, Pigments Department, Newark, N.J.

12. Chambers Works Chemical Control Department Monthly Summary, page 57, November, 1959.

13. Test Authorization TA-C-61-766 dated October 5, 1961 and the corresponding Test Conclusion, dated May 23, 1962.

14. Letter dated October 23, 1961 from A. W. Bilancioni, Technical Laboratory, to Mr. R. L. Burnett, Dyes and Chemicals Division.

15. Test Authorization TA-C-60-684 dated September 12, 1960 and the corresponding Test Conclusion, dated June 14, 1961.

16. Test Authorization TA-C-61-188 dated March 10, 1961 and the corresponding Test Conclusion, dated April 19, 1961.

17. Trial Manufacture Request TMR-C-57-81 dated August 14, 1957 and Part II dated August 28, 1957, and the corresponding Test Conclusion, dated February 19, 1958.

18. Interim Technical Standard, "Lithosol" Fast Violet 4RN Paste, authorized March 7, 1958.

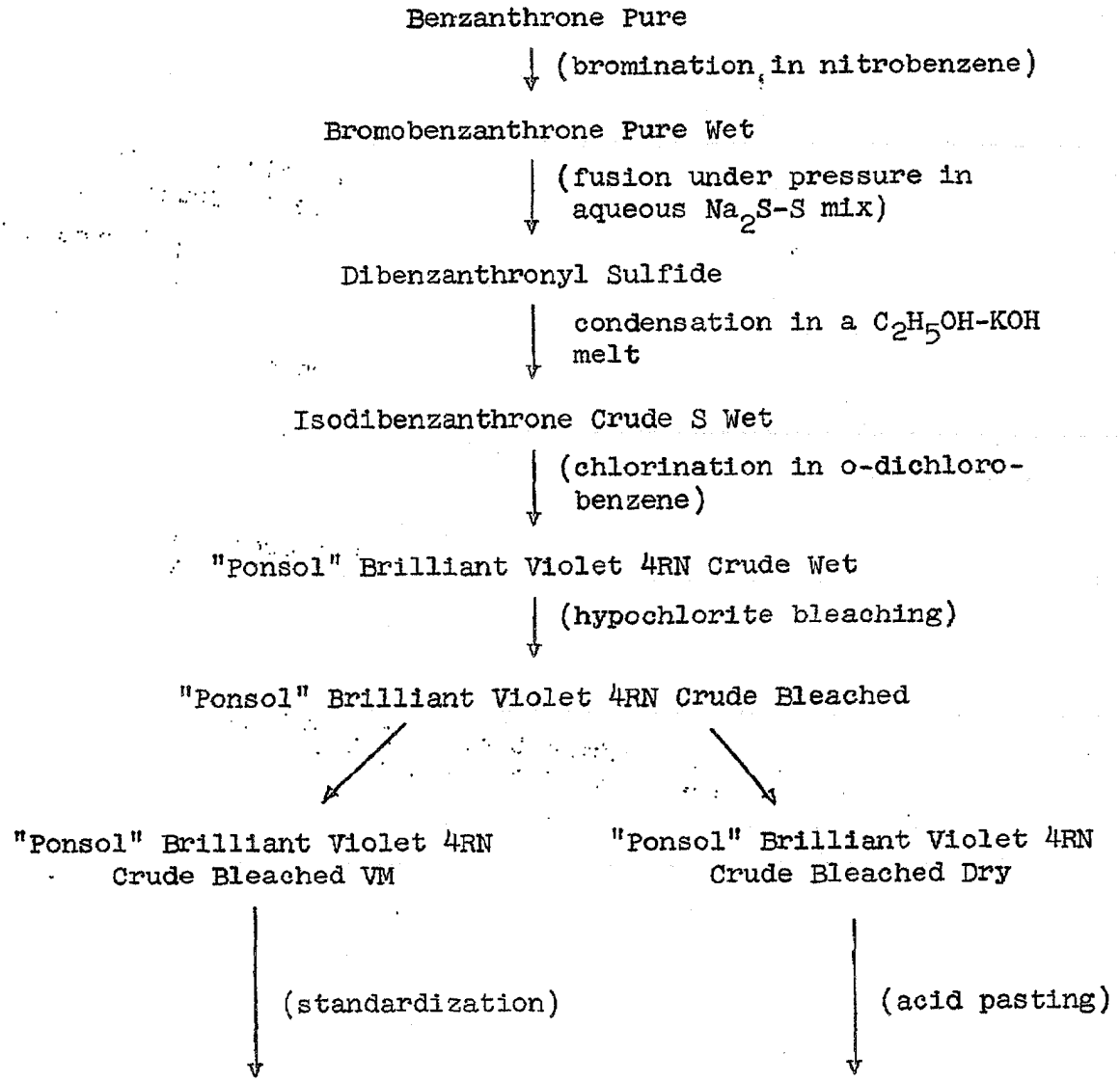
19. Test Authorization TA-C-59-981 dated December 22, 1959 and the corresponding Test Conclusion, dated February 7, 1961.

/ves

APPENDIX

APPENDIX 1

The following chart shows the steps involved in the current production of "Lithosol" Fast Violet 4RN Paste and "Lithosol" Fast Violet 4RNL Paste.



"Lithosol" Fast Violet 4RN Paste

"Lithosol" Fast Violet 4RN Paste Crude Acid

↓ (hypochlorite bleaching)

"Lithosol" Fast Violet 4RN Paste Crude

↓ (standardization)

"Lithosol" Fast Violet 4RNL Paste

For the textile trade, "Ponsol" Brilliant Violet 4RN Crude Wet is standardized to "Ponsol" Brilliant Violet 4RN Paste.

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