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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

KS-71 DIOXAZINE VIOLET: LABORATORY AND SEMI-WORKS PROCESS DEVELOPMENT

Period Covered: February, 1947 - July, 1949

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

Title: KS-71 Dioxazine Violet: Laboratory and Semi-Works Process Development

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I. INTRODUCTION

KS-71 "Dioxazine" Violet (2,9 diphenyl - 6,13 - dichloro triphendioxazine) was originally prepared by Dr. G. B. Robbins of the Jackson Laboratory. The product was described as about twice as strong as "Lithosol" Brilliant Violet 4RN, and much redder than the latter. A 90 CPU: 10 KS-71 Violet mix in lithographic varnish was intense and considerably redder than "Monastral" Fast Blue 2R (17% "Ponsol" Brilliant Violet 4RN +83% CPC co-acid pasted). This experimental dioxazine violet appeared to be redder, stronger, and better in lightfastness in linseed oil vehicles than Violet DX (3, 4, 10, 11 dibenz - 6,13 - dichloro-triphendioxazine) which at that time appeared to be the best shading color for CPC yet uncovered, but which was precluded from use due to its poor lightfastness in linseed oil vehicles and peculiar color change in baking enamels. Accordingly, laboratory studies on KS-71 violet were initiated by the New Organic Pigments Group of the Pigments Department at Jackson Laboratory in February, 1947 and continued until July, 1948 at which time the laboratory and semi-works process development studies were undertaken by the Newark group of the Pigments Department.

Laboratory and semi-works study on KS-71 "Dioxazine" Violet was discontinued in July of 1949 when extensive evaluations indicated that the pigment is sensitive to aromatic solvents, which behavior precludes its use in paint systems containing such thinners.

II. SUMMARY AND CONCLUSIONS

Laboratory and semi-works processes for the manufacture of KS-71 "Dioxazine" Violet have been developed and are outlined in the Appendices. Semi-works equipment and production experiences are described. A "one-solvent" process for KS-71 manufacture which appears attractive but which has not yet been fully investigated or evaluated is presented.

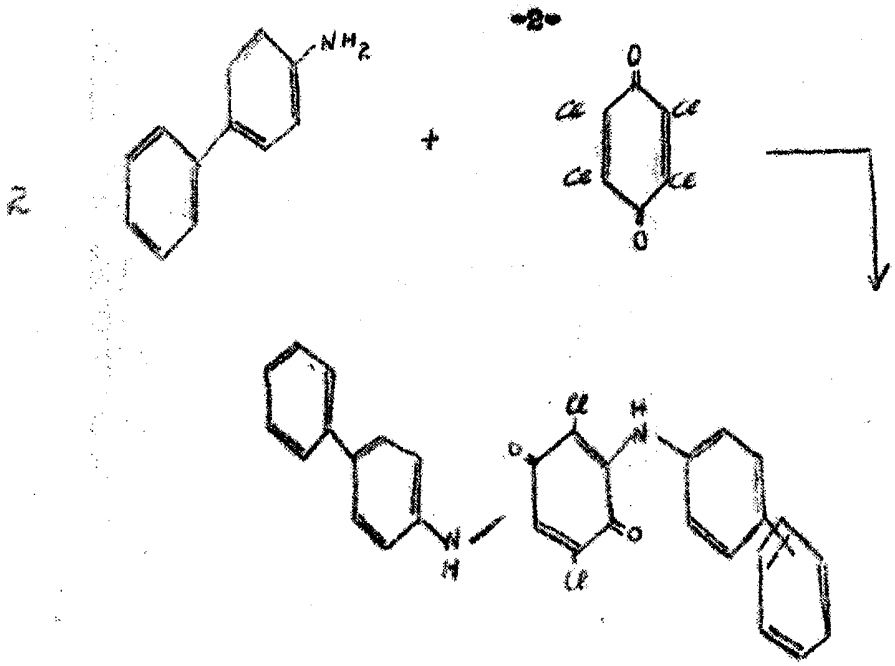
KS-71"Dioxazine" Violet exhibits a solvent instability and/or crystallization tendency in aromatic hydrocarbon solvents such as are used in several alkyd and lacquer formulations. Marked variations are obtained in tinctorial effects with change in solvents, principally with respect to dullness and weakness. These variations in hue were originally attributed to differences in flocculation and vehicle rather than to any deficiency in the toner pigment. Subsequent evaluation revealed the crystal growth characteristics of this pigment in aromatic solvents, and consequent hue and strength changes.

A summary of KS-71 Violet evaluation work in various applications is presented.

III. DISCUSSION OF RESULTS

1. "Dianilide" Intermediate

In the earlier stages of this development, the "dianilide" intermediate 2,5-di[p-phenyl anilido] -3,6 - dichloro - 1,4 - benzoquinone had been obtained in 96% average yield by the reaction of chloranil and p-amino diphenyl in either 2B ethanol or 10%, 80%, 90%, 90%, or 99% isopropanol respectively.



In all of the above procedures, sodium bicarbonate was used as an acid binder, and the reaction of chloranil with the amine appeared to be very rapid at temperatures between 50° and 70°C.

Subsequently, syntheses of the "dianilide" intermediate have been made in 5% and 10% isopropanol, respectively, and in water alone with magnesium oxide, and sodium acetate, respectively, as acid-binders. Initial attempts using the water process gave foaming difficulties which were not encountered in the dilute alcohol medium. On the basis of analyses, the purest products were made with sodium acetate as binder.

Synthesis of the "dianilide" intermediate in 5% acetone appears to proceed smoothly to yield 97-98% of isolated product. Sodium bicarbonate was used as the preferred acid-binding agent although soda ash could probably be used with equally good results. The "dianilide" intermediate has been coded ASF-39.

Subsequently, laboratory and semi-works study of intermediate (ASF-39) synthesis from chloranil and p-amino-biphenyl has shown that bicarbonate as an acid-binder presents serious foaming difficulties which can be avoided by using either disodium hydrogen phosphate or sodium acetate as binder. The latter agent is preferred. Yield with acetate was found to be quantitative (97% with bicarbonate). The use of 5% acetone for the synthesis of ASF-39 does not appear necessary based on laboratory runs in straight water. The latter runs returned equal yields in comparative runs using 5% acetone. Wetting agents in the straight water runs are unnecessary based on yield and quality data.

Accordingly, semi-works manufacture of ASF-39 intermediate has been confined to the aqueous process with sodium acetate binder, and without the use of wetting agent or solvent. The reaction is run in an open vat and the chloranil shoveled in dry when the charge of p-amino-biphenyl, sodium acetate, and water has been heated to 40°-75°C. The yield is quantitative and the intermediate was found to be easy to filter and wash.

A product equal tinctorially to Jackson Laboratory standard KS-71, but 20% strong after salt-milling, was produced in the first laboratory run at Newark from ASF-39 prepared with acetate in the semi-works as described above. The strength difference is explained by a 65-hour milling cycle versus a 50-hour cycle used earlier in Jackson Laboratory. Hypochlorite treatment of this finished product did not alter its tinctorial properties.

Seven lots of ASF-39 intermediate prepared in semi-works and checked for quality in laboratory KS-71 syntheses yielded satisfactory products within the acceptable laboratory limits. The yields averaged 41.8%. Only the first lot of ASF-39 prepared in the semi-works (lot 270) by the bicarbonate method, and which analyzed low for chlorine, yielded a product in low yield (31.9%).

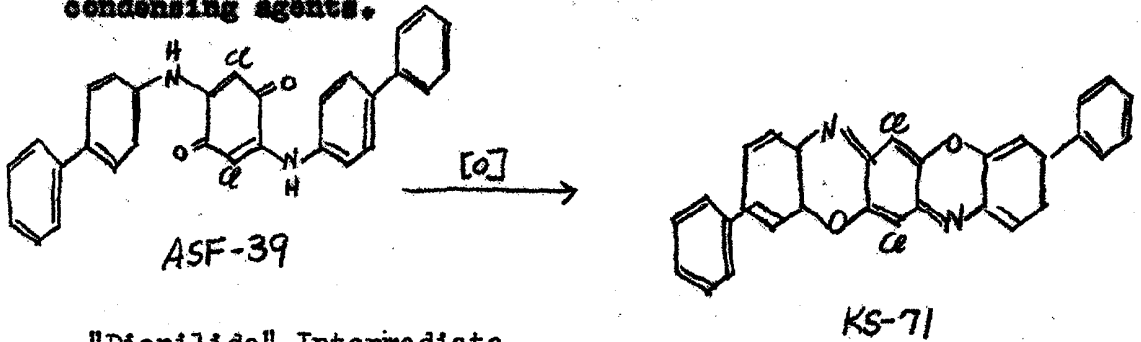
Some typical analyses for chlorine content of ASF-39 prepared in the semi-works are listed. The theoretical chlorine content is 15.89%.

Semi-Works Lot No.	% Chlorine
270	13.05
274	14.38
293	15.42
294	14.40
295	14.38
296	14.27
312	14.23
313	13.95
315	14.11
358	14.14
378	13.86

Laboratory and semi-works processes are described in the Appendices.

2. <u>"Dioxazine" Violet Formation; Ring Closure</u>

"Dioxazine" Violet is formed by ring closure of the ASF-39 "dianilide" intermediate in nitrobenzene medium in the presence of condensing agents.



"Dianilide" Intermediate

"Dioxazine" Violet

A rather detailed variable study was undertaken on ring closure in nitrobenzene using various combinations of catalysts. Some condensation to color occurs when the "dianilide" is heated in nitrobenzene alone, but the product appears to contain unchanged starting intermediate. When the "dianilide" is heated in nitrobenzene at 200°C. with PCl_5 and benzoyl chloride (original Jackson Laboratory procedure), or with PCl_5 and the equivalent of benzoyl chloride, e.g. p-toluene sulfonyl chloride, p-chlorobenzoyl chloride or p-nitro benzoyl chloride, an average yield of 88% (14 runs) was obtained. The remainder of the dianilide intermediate forms a black resinous material which is soluble in nitrobenzene giving a deep blue solution.

Substitution of $TiCl_4$ for PCl_5 in the regular procedure reduced yields to about 55% (average). Potassium permanganate substituted for benzoyl chloride gave a yield of 61%, while thionyl chloride in place of PCl_5 gave a yield of 66%. Iodine or ferric chloride gave no better yields than benzoyl chloride when substituted in the process for this acid chloride.

The use of mixed alkanesulfonic acids (Indoil Co.) as catalysts for KS-71 synthesis was not successful.

Consistent yields of 80% and higher were obtained with boron fluoride etherate [$BF_3 \cdot (C_2H_5)_2O$] alone and in conjunction with catalysts such as benzoyl chloride, PCl_5, potassium permanganate, and thionyl chloride in various combinations. A 90% yield of crude violet has been obtained in the laboratory using a combination of PCl_5, $KMnO_4$, and BF_3 etherate as catalysts. However, judged by salt-milled samples, the products of synthesis with thionyl chloride and boron fluoride-etherate, respectively, are very dull, brownish violets. A comparison of various samples of crude violet after salt-milling has shown that boron fluoride-etherate plus $KMnO_4$, sulfuryl chloride, sulfur pentoxy dichloride, and ferric chloride, or any combinations of these agents result in very dull and undesirable pigments tinctorially. Permanganate with PCl_5 and with or without benzoyl chloride does not harm the tinctorial properties of the violet, but the yield is not improved significantly over PCl_5 and benzoyl chloride alone.

Repeat runs, however, returned a 55% yield by permanganate substitution for benzoyl chloride as against 42% yield employing benzoyl chloride by "standard" process.

Salt-milling and bleaching of the various high-yield products obtained (mostly from BF_3 present in the ring-closure step) has given better tinctorial quality than that obtained without bleaching, but none of the products was equal to the KS-71 laboratory control either in intensity or strength. Selected high-yield products have been shown by Jackson Laboratory to yield very dull sulfur dyes.

Phosphorus oxychloride appears to be effective as a ring-closure agent in place of phosphorus pentachloride with no loss in yield. It appears the more desirable from a handling viewpoint, being a liquid at room temperatures. A sufficient number of runs have been made with $POCl_3$ in place of PCl_5 to show that a 8-10% yield increase is obtained.

Prior to semi-works development, the selected synthesis conditions for KS-71 Violet involved 24% "dianilide" intermediate by weight in nitrobenzene, ring-closure at 200°C. with $POCl_3$ and C_6H_5COCl for 5 hours, cooling by addition of dilute caustic soda to 90°C. (heat carried off in refluxing), filtration at 90°C., washing with nitrobenzene, steam-distillation to free of nitrobenzene, and drying. Yields on this procedure have averaged 50-55% of theory with no apparent differences in technique or procedure over previous runs which averaged 40% as crude. A laboratory check (3 runs) of the proposed plant ring-closure process returned yields of 43% as compared with the 50-55% goal yield. Four additional laboratory syntheses run essentially in accordance with the tentative plant process (4/26/43) (see Appendix VI) and using intermediate ASF-39 manufactured in the semi-works (acetate process, lot 274) gave an average yield of 49.67% (51.68%, 50.34%, 48.25%, 48.30%). To further check the synthesis yield, eight additional laboratory syntheses run in accordance with the tentative plant process (4/26/43) (see Appendix VI) using technical grade nitrobenzene and the solvent washing volumes specified, gave an average yield of 50.3% (48.4 - 54.6% yield range). The salt-milled products were distinctly red against KS-71b standard and varied considerably from run to run. It is significant that for the most part, higher yield was associated with poorer quality suggesting the need for complete and efficient solvent (nitrobenzene) washing of the synthesis mass so as to remove residual synthesis tars.

An additional series (3 runs) yielded only one product equal to KS-71b standard despite apparent completeness of washing in all cases. Further, exhaustive nitrobenzene washing of a finished inferior product gave little improvement in quality. It is evident that other factors inherent in the synthesis proper give rise to the erratic and inferior results obtained in this series.

A synthesis series using wet, technical grade nitrobenzene obtained by steam distillation without any further drying treatment, yielded products decidedly inferior to any of those previously prepared, despite complete nitrobenzene washing of the product. It is presumed that the presence of moisture during the synthesis is detrimental in that it either destroys the catalysts (acid chloride condensing agents) or in itself prevents completeness of reaction (i.e. ring closure) and/or gives rise to contaminating impurities. The need for anhydrous conditions and/or more catalyst (the latter can serve to remove water, and in addition may possibly enter into the reaction mechanism) was shown in a synthesis series run under anhydrous conditions using "topped" nitrobenzene and larger quantities of catalysts. The three salt-milled products checked each other well in contrast with the previously erratic series, and all were superior to KS-71b, being blue, intense, and strong against the standard. (Yields 40.8%, 43.2%, 40.8%).

Efforts were made to effect the ring closure reaction in o-dichlorbenzene and in trichlorbenzene using chloranil as oxidising agent, and in o-dichlorbenzene using air as the oxidising agent. Although good yields of beautifully crystalline crude products, superficially similar to those obtained by the nitrobenzene process, were obtained, the salt-milled products were decidedly unlike the standard, being of an almost entirely different hue (red-tan). Significantly, these materials unlike KS-71 (which does not melt up to 340°C.) melt

with decomposition at 325°C. ± 5°C., and impart an amber fluorescence in pyridine in which they are soluble to a considerable extent. KS-71 gives a reddish fluorescence in pyridine in which it is only very slightly soluble. The former product is apparently a different chemical entity which could well be an impurity in KS-71 and contribute to the tinctorial deficiencies of the inferior products. Subsequent treatment of one of these products with nitrobenzene and catalysts under synthesis conditions yielded a product in low yield approaching but not quite equal to the quality of KS-71b standard. It is postulated that these inferior materials represent incompletely reacted or ring-closed intermediates or mixtures of these intermediates with the completely ring-closed dioxazine, and that subsequent ring-closure can convert them to the dioxazine. Also, the amount of moisture and/or catalyst present during the syntheses determine the relative proportion of such intermediates present and ultimately, the quality of the pigment. The impurity appears to be soluble in pyridine and an inferior product so extracted proved to be bluer than standard, though duller. Also, pyridine extraction of one of the dichlorbenzene-synthesized products (red-tan material) yielded by pyridine extraction a relatively small quantity of a very much bluer material, presumably the ring-closed dioxazine.

The superior KS-71 Violet quality reported above (blue, intense, strong vs. KS-71b "standard", 41.4% average yield, 3 runs) was confirmed in an additional series of three runs (42.2% average yield). "Topped" nitrobenzene and larger quantities of catalyst were used. Another series (2 runs) using technical grade nitrobenzene without "topping", and larger quantities of catalysts likewise gave satisfactory products in 41.3% average yield.

Analyses of various inferior products indicate that these (red, dull, weak) have a low chlorine content (9.8 - 10.7%), whereas the satisfactory materials approach the theoretical chlorine content of "dioxazine" violet. It may be significant that the tars isolated from the synthesis slurry analyze in the range of 4.4% chlorine, and their presence may account for the low chlorine values in the inferior products.

Efforts to improve KS-71 synthesis yield by diluting the nitrobenzene with trichlorbenzene during synthesis did not give any appreciable yield change and excessive dilution of the nitrobenzene gave lower yields. In those syntheses where yields in excess of standard laboratory yields have been obtained, the products are decidedly undesirable tinctorially and probably are not wholly "dioxazine" materials.

Another attempt at yield improvement in the KS-71 synthesis involving the use of chloranil as an oxidising agent for ring closure, presumably to supplement the oxidising action of the nitrobenzene yielded a crystalline product in 62.2% yield. The salt-milled material was distinctly red against a "Dioxazine" Violet, and very intense. An additional synthesis series using chloranil in varying mole ratios and using larger quantities of catalyst yielded two products tinctorially similar to the above and in 44.8% and 57.6% yields for 0.5 mole and 2 moles of chloranil respectively. A synthesis using 1 mole of chloranil per mole of "dianilide" intermediate yielded a material in 64.0% yield. The salt-milled product was vvs blue and vvs weak against a

standard "dioxazine" product. The X-ray diffraction pattern of this material proved to be essentially identical with standard "dioxazine" materials whereas the X-ray diffraction pattern of the product reported to be distinctly red against a standard "dioxazine" product (0.5 mole chloranil excess per mole of dianilide intermediate in the standard nitrobenzene ring-closure) was unlike that of a characteristic "dioxazine" material.

A variable study of KS-71 synthesis as regards reaction temperature for ring closure suggests that the current 200°C. level is the optimum with respect to yield, versus 180°C. and reflux (approximately 218°C) levels.

3. "One-Solvent" Process for "Dioxazine" Violet

Initial attempts to prepare KS-71 by a simplified process involved the intermediate "dianilide" synthesis in nitrobenzene using sodium bicarbonate as acid-binder, cooling, adding the ring-closure agents, followed by condensation at 200°C. Yields of 60-65% crude have been obtained. One such product after salt-milling was weaker and duller (browner) than KS-71 laboratory goal. Soda ash can be used without loss of yield compared to bicarbonate in the formation of the intermediate in nitrobenzene, but substitution of caustic soda for bicarbonate gave a 20% lower yield of crude violet.

Further study of the "one-solvent" process returned yields of 55-60% using sodium acetate or bicarbonate as acid-binder, and phosphorus pentachloride and benzoyl chloride as ring-closure agents. The salt-milled products "as is" were all too dull to be of interest, but when bleached with alkaline hypochlorite after milling, red and intense violets were obtained compared to the original KS-71. Many of the "one-solvent" color slurries after reaction were practically unfilterable in laboratory, which serious deficiency would make a plant process inoperable.

One of the difficulties in the "one-solvent" process where the intermediate is synthesized in nitrobenzene, water removed by distillation, and the ring-closure performed in the usual way thereafter, has been shown up by syntheses of the "dianilide" in nitrobenzene under the above conditions. When sodium acetate was used as acid-binder, dechlorination of the dianilide was noted. Magnesium oxide gave a product containing almost the required amount of chlorine but only 90% yield was obtained. The remaining unreacted starting components may cause difficulty in the ring-closure step.

A "one-solvent" process based upon an I.G. "dioxazine" process as published in BIOS 960 was investigated. This process uses ODCB as solvent and excess chloranil as oxidant in the ring-closure process. The synthesis was attempted using (a) benzene sulfonyl chloride (as per the I.G. process), 73.8% yield, (b) benzoyl chloride, 68.3% yield and (c) $POCl_3$ plus benzoyl chloride, 45.8% yield. The salt-milled products have been found to be very dull and weak versus goal quality KS-71.

An initial attempt to synthesize the "dianilide" intermediate (ASF-39) for KS-71 in nitrobenzene medium at 100°C. and in the absence of an acid-binder, followed by ring-closure in nitrobenzene at 200°C. in the presence of catalysts (without prior isolation of the intermediate from the original nitrobenzene) yielded a green crystalline product in 40.1% yield and superficially similar to the "Dioxazine" Violet, but essentially of similar hue. Two additional syntheses using shorter heating cycles gave yields of 57% and 55% respectively.

The use of sodium acetate as an acid-binder during the "dianilide" synthesis phase of the reaction yielded a product in 26.6% yield. The final salt-milled product was of a hue entirely unlike that of "Dioxazine" Violet.

Rubout evaluation of a product prepared by the "one-solvent" process for KS-71 synthesis (34.5% yield) indicates that the material is satisfactory against a laboratory standard (s. blue, intense, equal strength). The X-ray diffraction pattern of this material proved essentially identical with characteristic "dioxazine" materials prepared in laboratory and in semi-works by the "two-solvent" process. The product was tinctorially superior to that prepared in the initial "one-solvent" process attempt.

4. Milling Studies

Salt-milling of KS-71 "Dioxazine" Violet crude yields a strong (about twice the strength of "Ponsol" Brilliant Violet 4RN), red and brilliant product.

No other method of particle-size reduction other than salt-milling has been found to be satisfactory. KS-71 cannot be acid-pasted since excessive sulfonation of the pigment occurs. One attempt to grind KS-71 crude in acetone under conditions found optimum for CPC failed to yield color of satisfactory strength, or shade. Further attempts in acetone under differing concentration conditions and for longer times than used previously were unsuccessful. The color failed to grind to satisfactory tinctorial properties in isopropanol, solvent naphtha, or in 40% sodium xylene sulfonate-water. In solvent naphtha the pigment developed strength but was very dull and blue versus the salt-milled sample. Attempts to grind in carbon tetrachloride or in methyl acetate were likewise unsuccessfull. The products were blue and distinctly weak.

Water-grinding of KS-71 crude using ammonia and Duponol WA as grinding aids failed to develop the desired strength and tinctorial properties of the color after as long as eight days of milling.

Attempts to grind KS-71 crude with salt in acetone failed to yield color anywhere near the tinctorial brightness and strength of the dry salt-milled product. Salt milling remains the only known practicable way of finishing this color.

A sample of KS-71 violet crude was salt-milled for 120 hours (50 hours was then standard salt-milling time in the laboratory) with no adverse effects on its tinctorial properties. The "over-milled" samples were slightly stronger and slightly bluer than KS-71.

Lightfastness of the colors milled 120 hours was equal to KS-71. The masstone skindown of this violet showed no fade after 100 hours fade-ometer exposure, and 1:100 zinc oxide tints faded only slightly after 50 hours exposure. This performance compares favorably with "Pensol" Brilliant Violet 4RN and is much superior, especially in tint, to the older Violet DX.

Salt-milling of KS-71 crude in a laboratory 0.65 gallon rigid steel mill yielded a product 13% weak and vs blue against the laboratory standard salt-milled in a quart can. Some caking was observed. Sodium sulfate grinding (quart can) yielded a product weak against a sodium chloride-milled control.

Salt-milling with and without wetting agents in the mill and/or in the extraction show no significant tinctorial differences in the finished product.

Salt-milling of Orchem semi-works synthesized KS-71 yielded a product essentially equal (vvs blue) to the Newark Laboratory temporary standard (1309-17B). The latter is bluer and more intense than lot #9415 KS-71, which material was used for the original KS-71 Violet evaluation work.

X-ray diffraction study of typical salt-milled violet indicate that milling in this way did not alter the crystal phase. The particle-size of the salt-milled material calculated from line-broadening appears to be about 1/4 to 1/3 that of CPC, namely from about 0.02 to 0.03 microns.

It has been shown that KS-71 violet is extremely sensitive to drying temperatures. When dried at 140°F., satisfactory pigment tinctorially is obtained. The pigments dried at 212°F. were excessively weak.

Laboratory and semi-works salt-milling procedures are described in the Appendices..

5. Hypochlorite Bleaching

Hypochlorite bleaching of KS-71 violet lot 9415 pulp yielded a product equal tinctorially to KS-71 laboratory goal. Approximately 12% loss in yield was obtained. Unbleached lot 9415 is very blue, and duller than the KS-71 goal.

Details of the laboratory procedure for hypochlorite bleaching are described in the Appendices.

6. "Dioxazine" Violet Lakes

The following lakes of KS-71 "Dioxazine" Violet have been prepared.

BF-279-D - A 50% aluminum benzoate lake of KS-71 Violet for paint use.

BF-315-D - A 50% lake of KS-71 "Dioxazine" Violet on Multiflex MM for printing ink use.

KS-135 - A"Ramapo"barium rosinated lake containing approximately 70% toner.

KS-136 - A 50% aluminum benzoate lake of a blankophor treated KS-71 Violet (barium salt of the blankophor to the extent of 5% of the Violet toner).

KS-137 - A 50% aluminum benzoate lake of a KS-71 Violet "Ramapo".

KS-138 - A 50% aluminum benzoate lake of a hypochlorite - bleached KS-71 Violet.

KS-130 - A 14% lake of KS-71 Violet on alumina hydrate prepared by the BP-176-D formula.

KS-132 - A 9.6% lake of KS-71 Violet on whiting prepared by the BP-263-D formula for linoleum application.

Linoleum lakes containing 10, 15, and 20% KS-71 Violet (resinous oil, whiting) appear to be satisfactory strengthwise and colorwise as a self-color and as reddening agents for CPC linoleum lake BL-283-D.

7. Semi-Works Process Development

a. Early Semi-Works Development

Forty-four pounds of "dianilide" intermediate was prepared by reaction of chloranil with p-amino biphenyl using sodium bicarbonate as acid-binder, and 80% isopropanol as solvent. An overall yield of 87% of dry product was recovered from ten small runs (laboratory yield 96%) but considerable product was lost in handling.

Forty pounds of the above "dianilide" was ring-closed in 13 gallons of nitrobenzene using 5 pounds of benzoyl chloride, 5 pounds of phosphorus pentachloride, and 1 pound boron-fluoride etherate as condensing agents. A yield of 50% (comparable to laboratory results under the same conditions) was realized, and 18 pounds of crude crystalline violet was obtained after filtration, washing of crude with nitrobenzene, and vacuum drying to remove nitrobenzene solvent.

Attempted salt-milling of five pounds of the crude violet prepared as above in a 25 gallon Newark mill failed due to severe packing.

Laboratory salt-milling of the semi-works crude violet yielded a product slightly duller and weaker (15-20%) than the original laboratory-synthesized standard.

One salt-milling of this color in the Jackson Laboratory semi-works 50 gallon mill yielded a product (lot 9418) equal in strength to the laboratory goal KS-71, but appreciably bluer than the latter after grinding 30 hours. The blueness was attributed to contamination with CPC blue. An additional milling yielded a product (lot 9418) close to the laboratory goal, but still slightly blue when milled for 36 hours. These grinds were made at a salt-pigment ratio of 6:1 which is probably considerably higher than required for plant scale millings judged by experience with phthalocyanines.

Subsequent development work in the semi-works on ASF-39 indicated sodium acetate to be the desirable acid-binder as compared to sodium bicarbonate. A run using sodium bicarbonate in 5% acetone foamed severely, and a 75% yield was obtained (losses were mostly mechanical). A comparative run made with sodium acetate and no acetone proceeded smoothly and returned a quantitative yield.

The first increased batch size of ASF-39 (600 lbs.) completed in the semi-works returned a 97.5% yield. The product analyzed for 14.14% chlorine. A second batch returned a 98.4% yield.

The KS-71 Violet process run in semi-works in accordance with the tentative plant process (4/28/48) (see Appendix VI) gave no difficulty in the synthesis step proper. Filtration, however, yielded a presscake containing approximately 25% solids as against 65% presscakes obtained in the laboratory. Nitrobenzene washing in the filter press did not prove as effective as in laboratory, presumably due to channeling. As a result of incomplete nitrobenzene and tar removal, the subsequent steam distillation step gave rise to severe pelleting of the crude violet. Laboratory study of these crude pellets indicated that they could be easily dispersed in hot nitrobenzene and finished as usual. The salt-milled product so obtained was redder than standard KS-71b. If, however, the pellets are redispersed in hot nitrobenzene under synthesis conditions (i.e. anhydrous conditions, and phosphorus oxychloride and benzoyl chloride catalysts), a product (salt-milled) is obtained which is strong, blue, and intense against standard KS-71b.

Difficulties experienced in the past with the filtration of the hot nitrobenzene reactor slurry have been largely overcome by the use of Orlon filter cloths on the press. Orlon which weighs 18 oz. per yard shows none of the tearing, and jellying characteristics of nylon, vinyon and cotton in this service. Solids contents of the nitrobenzene presscake have averaged 45.5% and the bulk density of the crude violet has been 22.8 lbs./cu. ft. of press volume.

It appears that successful washing of the presscake in the press with fresh hot nitrobenzene is feasible without an intermediate reslurrying and refiltration step, although the quantity of nitrobenzene needed for the press-washing may be excessive. The choice of method to be used for tar removal is an economic one, in which the cost of nitrobenzene recovery is balanced against the cost of double handling of the presscake.

The details of some early semi-works production are tabulated:

Batch No.	Estimated Yield, Lbs.	Lump Yield Lbs.	Overall Nitrobenzene Usage, lbs./lb. pigment	Quality (Extension of Lab. Standard
357	25.2	21.0	55.1	=, red
360	25.2	18.5	57.0	v.s. wk, dull
362	25.2	22.0	22.6	wk, vs dull
363	25.2	24.5	45.6	=
364	23.8	-	28.9 (approx.)	-

The overall crude violet yield for the month was 87.6%.

b. Nitrobenzene Distillation

Removal of residual nitrobenzene from the presscake has been accomplished successfully by steam distillation in alkaline medium. No evidence of pelleting has been observed. The cycle time appears to be well under 12 hours per synthesis charge.

c. Tar Removal

Semi-works efforts to effect maximum tar removal from the crude KS-71 by press washing were concentrated on increased dilution of the hot reactor slurry with additional nitrobenzene (200 lbs. instead of 50 lbs.) prior to filtration. Also, the lines and press were flushed with hot nitrobenzene immediately before pressing to preclude the possibility of plugging the press ports with crystallized material as would probably occur on pumping the hot slurry into the cold lines and press. The material filtered very well and washed rapidly, indicating considerable improvement. Laboratory evaluation of the individual presscakes of this lot showed satisfactory uniformity, whereas the evaluation of previous presscakes disclosed large quality variations.

d. Salt-Milling

Salt-milling of crude KS-71 has been successfully carried out in the 25 gal. mill with standard strength obtained after 12 hours of milling. In all cases the mill was loaded with 300 lbs. of mixed 1/2" and 1" balls, 220 lbs. of salt, and 3 lbs. of crude KS-71. In the first grind 30 lbs. of roofing nails were also put into the mill to prevent "caking" on the mill walls. However, a subsequent trial without nails indicated that a negligible amount of caking developed. In all grinds 100% discharge was obtained.

In the foregoing salt milling work both the salt and the pigment were dried at 110°C. prior to loading into the mill, which fact may account for the absence of caking. The maximum temperature reached in the mill was 210°F., there being no water-cooling used.

Loading for the 276 gallon mill has been increased from 33 lbs. to 50 lbs. of crude KS-71 with no increase in milling time necessary to attain standard quality.

The use of a modified mill discharge cover has made possible 100% discharge of mill contents in approximately 40 minutes, with negligible dust conditions. Inspection of the mill interior after each grind has disclosed no evidence of "caking".

The general quality of semi-works material has been good, being somewhat on the red side of laboratory products. Yields averaged 44.3% (41.5% previously).

e. Acid Extraction

Efforts directed toward reduction of the 14 hr. press washing time per batch (20 lbs. color and 110 lbs. NaCl) were made by using a modified method of press filling and washing. It has been possible to reduce the overall filling and washing time from 16 hrs. to 1 hr. The method comprises continuously diluting the slurry during the first 15 minutes of pressing, following which the dilution is discontinued and the vat allowed to pump empty. The vat is then filled with hot water

(170°F.) which is pumped into the press thru the slurry line. Approximately 300 gals. of water per 20 lbs. of color has been arbitrarily used. Subsequent to the hot water wash, cold water is run into the press thru the wash lines for approximately 10 minutes, at which time the filtrate is substantially chloride and sulfate free (7,000 to 15,000 ohms). This performance has been successfully repeated several times and the method will henceforth be considered standard.

As a result of a close study of the crude filtration step, it has been possible to reduce the nitrobenzene consumption per pound of color from 45¢/lb. to 18¢/lb. - a 60% reduction saving approximately $154.00 per 57 lb. batch.

One batch of KS-71 was synthesized to provide material for a nitrobenzene washing study. The batch was split before filtration and one half was press washed with 25 lbs. of nitrobenzene per pound of color, while the remaining half was press washed with 18 pounds of nitrobenzene per pound of color. KS-71 which had been washed in semi-works with the larger quantities of nitrobenzene so as to remove more synthesis tars proved to be slightly bluer and more intense than the lesser-washed control. When evaluated as the aluminum benzoate lake, however, the product behaved similarly to the lesser-washed control as regards strength loss and color deterioration in aromatic solvent enamel and lacquer systems.

8. Lakes of KS-71 "Dioxazine" Violet with CPC Blues

In order to match BP-243-D "Pocono" Blue, a series of "Ramapos" were prepared using KS-71 toner pulp (BT-309-D) and LB/CPC toner pulp (N-625) mixtures. The desired degree of redness was obtained at a KS-71/LB-CPC pigment ratio of approximately 12/88. A considerable strength advantage was apparent, as well as some dullness. An additional series employing acid-pasted chlorine-free CPC ("Monastral" Blue R) indicated that the desired redness could be obtained at a 10/90 pigment ratio of KS-71/CPC.

An alkyd enamel prepared from a KS-71/LB-CPC "Ramapo" (15/85 ratio) designed to match a BP-243-D enamel proved to be redder and considerably stronger than BP-243-D at equal pigmentation. Extension with 20% of TiO_2 yielded an enamel of equivalent strength versus BP-243-D. No significant difference in bleed (white over-stripe) was observed after baking (30 minutes at 265°F.).

Additional alkyd enamel blends of BP-279-D (KS-71 aluminum benzoate lake) and BT-284-D designed to match BP-243-D (at 10/90 and 2/98 extension levels) indicate that a fair match strengthwise and colorwise can be obtained at a pigment ratio (KS-71/LB-CPC) of 11.7/88.3 as compared to a ratio of 15.7/84.3 for a Violet 4RNL/LB-CPC blend. Money values are discussed in detail in a letter (F. F. Ehrich to F. A. C. Wardenburg, 6/2/49).

In order to obviate some of the flocculation objections inherent in the "Ramapo" consisting of a blend of LB/CPC toner and KS-71 toner pulp and designed to match BP-243-D, a blend of LB/CPC toner and the aluminum benzoate lake of KS-71 (BP-279-D) was prepared. The 25% blend

fixe extended product (ABP-315-D) showed no major improvement in flocculation behavior against the "Rampo" as regards hue change accompanying flocculation.

Blends of BP-279-D (KS-71 aluminum benzoate lake) with BL-282-D (KB/CPC aluminum benzoate lake) to match BP-245-D tinctorially and designed to overcome the objectionable flocculation and color deterioration observed with blends of BP-279-D with BT-284-D in enamel and lacquer systems were no more satisfactory than the latter.

A linoleum lake consisting of 75% whiting and 25% of a 15:85 blend of KS-71 Violet and KB/CPC has been coded BL-306-D.

9. Evaluation Work

The following description of KS-71 Violet was accepted prior to the undertaking of the semi-works development at Newark.

1. Very strong (approx. 2-1/2 BP-275-D) red-shade violet. Money value $45.00 vs. BP-275-D.

2. Lightfastness in fadeometer and outdoors exposure in alkyd enamel (3 mos. Florida) equal to CPC.

3. Durable in alkyd enamel (3 mos. Florida).

4. Mechanically blendable with CPC blue to give red shade blues of good intensity. 7% KS-71 + 93% BP-173-D = match for BP-293-D in litho varnish. 77-1/2 parts ~ 100 parts BP-245-D. Value $61.74/lb.

5. Non-bleeding in air dried film, slight bleed in baked vehicle (white overstripe). Stable to bake at 275°F.

6. Satisfactory in reactivity after one month shelf storage in alkyd enamel.

7. Flocculates in paint-vehicles when extended with TiO_2 (similar to CPC).

8. Migrates in vinyl film.

A 1:100 KS-71 Violet tint in zinc oxide faded only slightly after 135 hours exposure, and masstone skindown showed no break in the same time. The color bled only slightly in linseed oil (white paint overstripe, 140°F. bake), and less than "Pensol" Brilliant Violet 4RN. In soap (sandwich test), the "dioxazine" violet bled slightly (brownish stain) but less than the control "Pensol" Brilliant Violet 4RN.

Evaluations of KS-129, 50% aluminum benzoate lake of KS-71, lot 9415, showed that this lake is relatively non-flocculating in alkyd enamel/TiO_2 systems. Furthermore, mixtures of KS-129 and an aluminum benzoate lake of CPC blue gave red-shade blues which were also non-flocculating in alkyd. KS-129 was intense and apparently stronger than indicated by color content compared to KS-71 lot 9415 toner in alkyd.

Alkyd enamel and lacquer evaluations of a KS-71 aluminum benzoate lake wholly manufactured in semi-works in good yield, indicated the product to be tinctorially superior (red, trace strong) to a laboratory counterpart, and decidedly superior to the aluminum benzoate lake on which the initial KS-71 evaluations were made (red, intense, equal resistance to flocculation as shown by rub test).

The hue and strength changes observed when KS-71 toner or the aluminum benzoate lake (BP-279-D) are used in paint systems suggest the varying sensitivity of these colors to different paint thinners. The degree of tinctorial change (dullness, strength loss, etc.) appears to depend on the aromatic hydrocarbon content of the paint thinner, being greatest in xylene, intermediate in Amsco B (72-75% aromatic), and least in mineral spirits or VM and P naphtha. The color change is likewise observed in lacquer systems. The effect may be due to any one or combination of the following factors:

1) presence of nitrobenzene soluble impurities (synthesis tars).
2) varying degrees of flocculation in different solvents.
3) slight solubility of KS-71 in aromatic solvents.

The last appears to be the most likely factor.

An attempt to minimize the hue change by forming a protective film (sodium carboxy methyl cellulose) over the pigment surfaces was not successful.

The linoleum lake of KS-71 violet, lot 9415, on whiting, (KS-132), dispersed readily and gave an intense red shade blue with BP-263-D compared to the usual blends of the latter with the azo red RM-545-D. KS-132 was found to be soapfast and lightfast. Blends of KS-132/BP-263-D were more lightfast than RM-545-D/BP-263-D mixes of approximately equal hue.

Evaluation of the various lakes ("Ramapo", benzoate lakes, hydrate) of KS-71 showed that none were significantly different from ABP-279-D (50% aluminum benzoate lake of KS-71) in their properties in paints, linoleum, vinyl and rubber. All migrated severely in rubber and vinyl plastics.

Both weathered and "under glass" direct sunshine exposure of linoleum panels pigmented with KS-71 (whiting lake, KS-132) both "as is" and in combinations with BP-175-D showed KS-71 to be much superior in lightfastness to RM-545-D as a shading color in linoleum, and essentially equal to CPC in fastness. Earlier fadeometer results were confusing and contradictory in that little superiority over RM-545-D was evident as judged by fadeometer exposure.

An attempt to grind crude KS-71 in alkyd enamel failed to develop the desired strength, and in addition the tints were very dull. One interesting observation has been made with the masstone panel of this alkyd paint made from crude, viz. the crude fluoresces in ultra-violet as a toluidine red shade. None of the salt-milled violets shows much, if any, fluorescence.

EVALUATION REPORTS

RLM-2527, K
RLM-127, 5/28/47 S-7088

GE-2527, Mineral Spirits. Eval. of KS-71 toner.
2.5 stronger than Platinum Violet. Showed baked bleed and severe flocculation. Product rated of interest tinctorially. Later assessment of exposures returned excellent durability and L/F in tints and metallics. Severe bronze in heavy shades.

Newark N.B. 1230-68, 95, 104

GE-2527, Mineral Spirits. KV-36 Lacquer
KS-129 (later ABP-279-D) Aluminum benzoate lake.
Rated non-flocculating in alkyd
Lacquer spray cuts: duller and weaker than alkyds. Noted but not emphasized. Difference assumed to be due to differences in vehicle.

RLM-48-3 3/4/48

KS-132, whiting lake of KS-71, in linoleum.
Blend with BP-263-D showed superior L/F to BP-263-D/RM-545-D blends.

S-7126 1/12/48

GE-2527, Mineral Spirits.
BP-173-D shaded with KS-71 - tints only.
KS-71 slightly inferior in color retention compared to BP-173-D. In blends where KS-71 was present in the ratio 5 parts KS-71/95 parts BP-173-D, L/F was definitely inferior and gloss retention inferior to even KS-71 itself.

S-7139 3/8/48

GE-2527, Mineral Spirits
ABP-279-D and KS-71 Violet as shading colors compared to Platinum Violet (BP-275-D).
KS-71 was slightly reactive in the grind and showed poor gloss at all tint levels higher than 30/70 color/white.
KS-71 and BP-279-D bronzed more than BP-275-D at every level.

RLM 48-4 April, 1949

GE-2527, Mineral Spirits.
Flocculation Study KS-71 vs KS-129 (ABP-279-D)
KS-71 flocculation with TiO_2 in blends with GPC and in greys.
ABP-279-D does not flocculate and does not exert any beneficial effect in systems which do flocculate.

RLM 48-13 5/5/48 S-7143

Miscl. Lakes, etc. of KS-71
GE-2527, Mineral Spirits

KS-129 (ABP-279-D) selected as most practical for paint evaluations and then only where the tendency to bleed and to bronze is not considered undesirable.

RLM 48-14 5/5/48

Miscl. Lakes, etc. in linoleum.

RLM 48-15 5/12/48

Miscl. Lakes, etc. in Vinyl.
KS-71 Violet is no good as a vinyl color.

RLM 48-16 5/12/48

Miscl. Lakes etc. in rubber
KS-71 Violet migrates

RLM 48-20 6/22/48

KS-132 lake in linoleum
Outdoor and fadeometer exposures

RLM 48-30 9/3/48

Outdoor exposures of KS-132 in linoleum.
Certain anomalies occurred in the linoleum evaluation. It all amounted to rather poor cure resistance for KS-132. Depending on the degree of curing, KS-132 was reported superior to or inferior to BP-263-D/RM-545-D blends.

S-7170 9/13/48

ABP-279-D in GE-2527, Mineral Spirits
GE-2462/Resimene, VM & P
KV-36 Lacquer
Difference in tinctorial properties and strength noted between GE-2527 and GE-2462 systems. Again attributed to differences in vehicle, wetting etc.

S-10038 8/8/49

GE-2527, Mineral Spirits
ABP-279-D

RLM 49-32 12/7/49

KS-71 in refrigerator enamels
Almost complete fadeout on baking.

RLM 49-28 8/29/49

BP-279-D alkyd evaluation
GE-2527, Mineral Spirits
In blends with BT-284-D to approximate BP-243-D, the

combinations employing BP-279-D were slightly dull, while those with BP-273-D were slightly red. BP-273-D seems to be more compatible with BT-264-D in blends than does BP-279-D since the redness of BP-279-D produces a "flash" resulting in dullness.

PTSR #11 5/18/49

F & F, Philadelphia, criticized ABP-279-D for lack of "flash" (two-tone) in metallized enamels. No criticism of tinctorial instability.

PTSR #29 6/23/49

Parlin uninterested in ABP-279-D because of dullness and lack of "flash".

GLM #51 6/9/49

BL-308-D (15/85 KS-71/CPC blue lake) vs RM-545-D/BL-288-D in linoleum.

The lightfastness (fadeometer) and heat stability is inferior to RM-545-D/BL-288-D blends. It showed no advantage in soap and alkali resistance. It was more expensive to use.

S-7155 to 7160 6/49

KS-71 tinctorial variations from vehicle to vehicle due to solvent sensitivity and/or crystal growth.

SSR-52-1, Work Request G-17

Bimini Blue. Blends with BP-279-D are dull, lack "flash", but attractive costwise.

RLM 49-38 8/1/49

Crystal Growth Study of KS-71 Violet. KS-71 Violet behaves differently in alkyd enamels thinned with different thinners such as xylene, VM & P Naphtha, Mineral Spirits or Amsco B. This behavior which amounted to a dulling of the masstone color as different solvents were used suggested either crystal growth and/or flocculation. Xylene, from which KS-71 can recrystallize is the worst offender.

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   Ltr. D. B. Killian to F. F. Ehrich - 7/1/48.

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   Ltr. L. B. Magruder to D. B. Killian - 7/19/48.

5. "KS-71b, Salt-Milled Diphenyl Dioxazine Violet"
   Ltr. D. B. Killian to F. F. Ehrich - 8/5/48.

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   Ltr. D. B. Killian to L. B. Magruder - 9/16/48.

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    Ltr. U. S. Rubber Co. to F. F. Ehrich - 11/24/48.

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    Ltr. Monsanto Chemical Co. to F. F. Ehrich - 12/6/48.

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    Ltr. L. B. Magruder to D. B. Killian - 12/21/48.

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    Ltr. L. B. Magruder to D. B. Killian - 1/4/49.

17. "Filter Medium for Crude Violet"
    Ltr. L. B. Magruder to D. B. Killian - 1/7/49.

18. "Nitrobenzene Vapor Survey"
    Ltr. L. B. Magruder to D. B. Killian - 1/26/48.

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22. "Estimated Mill Cost for KS-71 Violet at 14,400 Pounds Per Year"
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27. "Cost Analyses - KS-71/CPC Ramapo"
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1168

1246

1255

1256

1288

1309

1333

APPENDIX I

LABORATORY PROCESS FOR PREPARATION OF "DIANILIDE" INTERMEDIATE (ASF-39) FOR FS-71 VIOLET SYNTHESIS

To a 10 liter jar provided with wood-paddle agitation, steam tube, and thermometer, add

water	3.5 liters
p-amino biphenyl	338 gr.
sodium acetate	164 gr.

Heat to 40°C. with good agitation and add slowly over a 10 minute period
246 gr. of chloranil slurried in 1.5 liters of water

Heat slowly to 90°C. and maintain at 90° ±2°C for 3 hours.
Cool to 60°C. by flooding with water.
Filter
Wash chloride free
Dry at 100°C.

Yield 508.7 gr. = 99.5% theory.

APPENDIX II

LABORATORY PROCESS FOR SYNTHESIS OF XS-71 "DIOXAZINE" VIOLET

Place in a one-liter glass reactor
150 gr. "dianilide" intermediate (ASF-39)
400 ml. nitrobenzene (tech.)
20 ml. phosphorus oxychloride
15 ml. benzoyl chloride

Heat to 200°C. and maintain at 200° ±3°C for 5 hours
Filter hot
Wash with 2 - 1000 ml. portions of nitrobenzene at 110°C.
Steam distill the nitrobenzene presscake in the presence of a solution of 20 gr. of sodium carbonate in 2 liters of water
Filter hot
Wash free of alkali
Dry at 100°C.
Yield 66.2 gr = 44.5% theory

LABORATORY

APPENDIX III

LABORATORY "ONE-SOLVENT" PROCESS FOR SYNTHESIS OF FS-71 "DIOXAZINE" VIOLET

Place in a one-liter glass reactor:
99.5 gr - p-aminobiphenyl
72.2 gr - chloranil
500 ml. nitrobenzene (tech.)

Heat to 100°C ±5°C. for 4 hours
Cool to room temperature
Add 20 ml. phosphorus oxychloride
15 ml. benzoyl chloride
Heat to 200°C.
Maintain at 200° ±5°C. for 5 hours
Filter hot.
Wash with 2 - 1000 ml. portions of nitrobenzene at 110°C.
Steam distill the nitrobenzene presscake in the presence of a solution of 20 gr. of sodium carbonate in 2 liters of water.
Filter hot
Wash free of alkali
Dry at 100°C.
Yield 59.6 gr. = 40.1% theory

APPENDIX IV

LABORATORY SALT-MILLING OF KS-71 VIOLET CRUDE

Place in a one-quart friction top can:

15.0 gr. KS-71 Violet crude (oven-dried at 100°C.)
100 gr. NaCl (oven-dried)
1500-1700 gr. mixed 1/4" - 1/2" steel balls
100 - 200 gr. roofing nails.

Grind for 60 hrs.
Screen pigment-salt mix from steel balls
Extract pigment-salt mix with 80 ml. of a 1:1 sulfuric acid solution diluted to 1500 ml. with water. MP-189 or Duponol facilitates the wetting of the pigment-salt mix.
Heat to 75 ±5°C. and maintain for 1 hour.
Filter hot, wash free of chlorides and dry at 140°F.

APPENDIX V.

LABORATORY HYPOCHLORITE TREATMENT OF KB-71 VIOLET

18 gr. KB-71 violet
420 ml. water
3.5 gr. $NaHCO_3$
3.5 gr. 13% NaOCl

The sodium hypochlorite solution is added to the pigment slurry at 80° ±0°C. at such a rate that a starch - KI test is positive at all times.
Filter hot, wash alkali - free.
Dry at 140°F.

APPENDIX VI

KS-71 VIOLET-TENTATIVE PLANT PROCESS
(D.B. KILLIAN 4/26/48)

1. **Synthesis of Intermediate**

Input:
- 5,000 lbs. H_2O
- 250 lbs. acetone
- 338 lbs. p-amino biphenyl
- 246 lbs. chloranil
- 168 lbs. sodium bicarbonate

Total 6,002 lbs.

Output:
- 496 lbs. product (100% basis) 97% yield
- 5,506 lbs. waste to sewer.

PROCEDURE:

Charge all ingredients to kettle except chloranil.
Stir. Heat to 40°C. Charge chloranil as slurry from tank in 45 min. - 1 hr. (Caution!)
Foaming
Heat to reflux 91°C.
Reflux 2 hrs.
Flood with cold water to 60 ±5°C.
Filter. Wash chloride free.
Press cake averages 35% solids
Dry at 100°C.
Note: Chloranil is slurried with 1000 - 1500 lbs. of the starting 5000 lbs. water.

Remarks: During initial stages of the reaction, the reactor mass stiffens and partially "sets" as a thick paste. This thins out to a fluid slurry on refluxing.

2. **Synthesis of Crude Color**

Input:
- 450 lbs. "dianilide" intermediate
- 2,600 lbs. nitrobenzene
- 50 lbs. phosphorus oxychloride
- 37 lbs. benzoyl chloride
- 60 lbs. soda ash

Output:
- 245 lbs. KS-71 crude
- 2,600 lbs. nitrobenzene to recovery
- 292 lbs. tar, etc. to waste
- 60 lbs. soda ash to waste

PROCEDURE:

Charge dianilide, and 1400 lbs. nitrobenzene. Add liquid $POCl_3$ and benzoyl chloride. Heat to 200 ± 10°C. Hold on temperature 5 hrs. Cut heat. Add ±1200 lbs. cold nitrobenzene to 80 ±5°C. Filter, wash with nitrobenzene, blow cake. Nitrobenzene to steam still for recovery.

Charge cake to steam still plus 60# soda ash. Add water as required. Steam distill free from nitrobenzene.
Filter wash.
Yield = 245 lbs. (55%)
Solids content of cake = ±50%

Note: HCl is evolved during synthesis.

3. Finishing Violet Pigment

Salt-Milling

Charge: 200 lbs. RS-71 Violet Crude
1,200 lbs. oven-dried salt
12,000 lbs. mixed balls (1" - 1/2" - 1/4")

Cycle: 30 hrs.

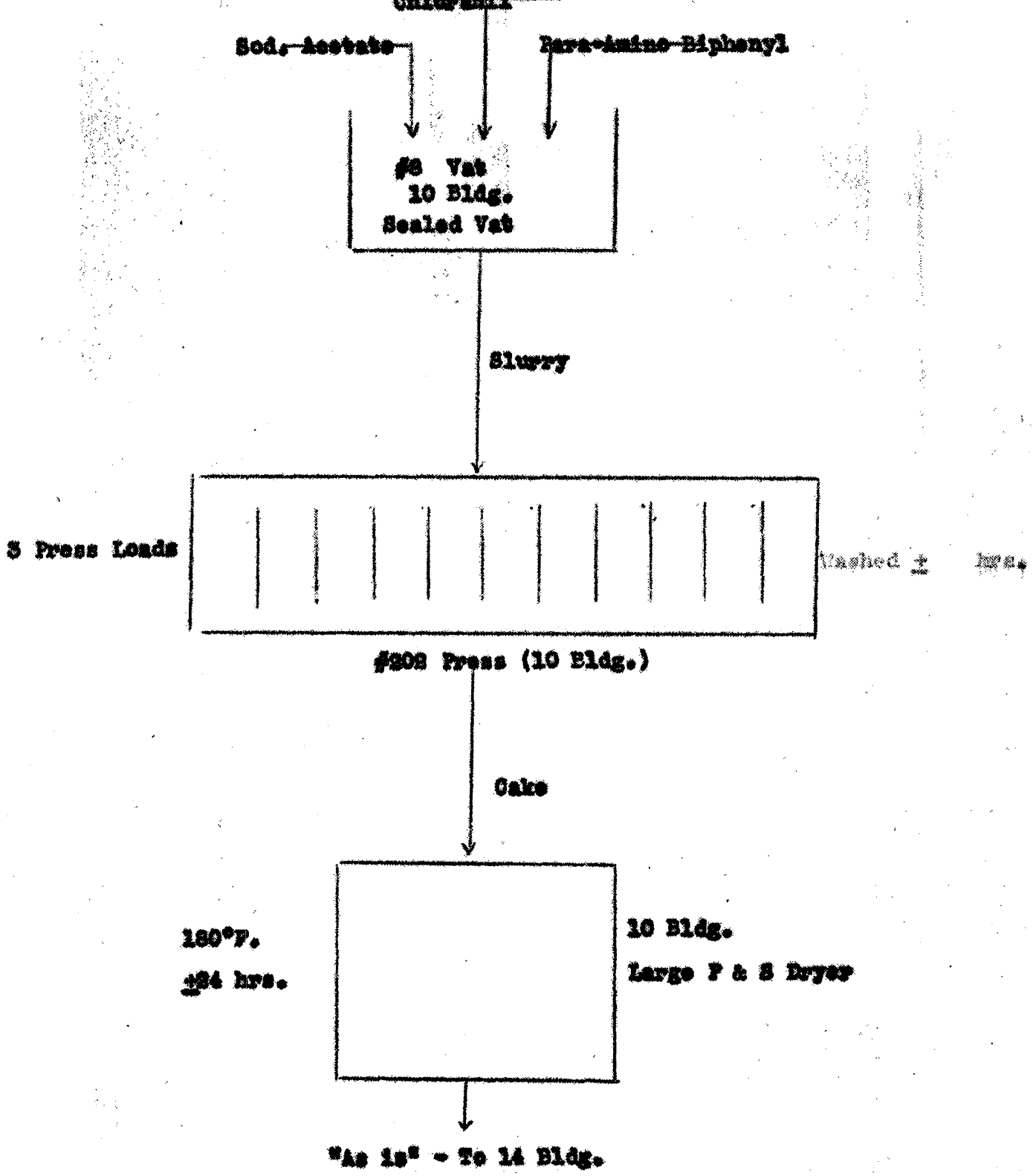
PROCEDURE

Charge ingredients to dry ball mill. Grind 30 hrs. Discharge as dry crude. Feed crude into vat containing 7500 lbs. of 2.5% sulfuric acid. Heat to 75 ±5°C. and hold on temperature for 2 hrs. Filter. Wash chloride free. Blow cake. Pack presscake as standardized pulp (20% solids).

APPENDIX VII

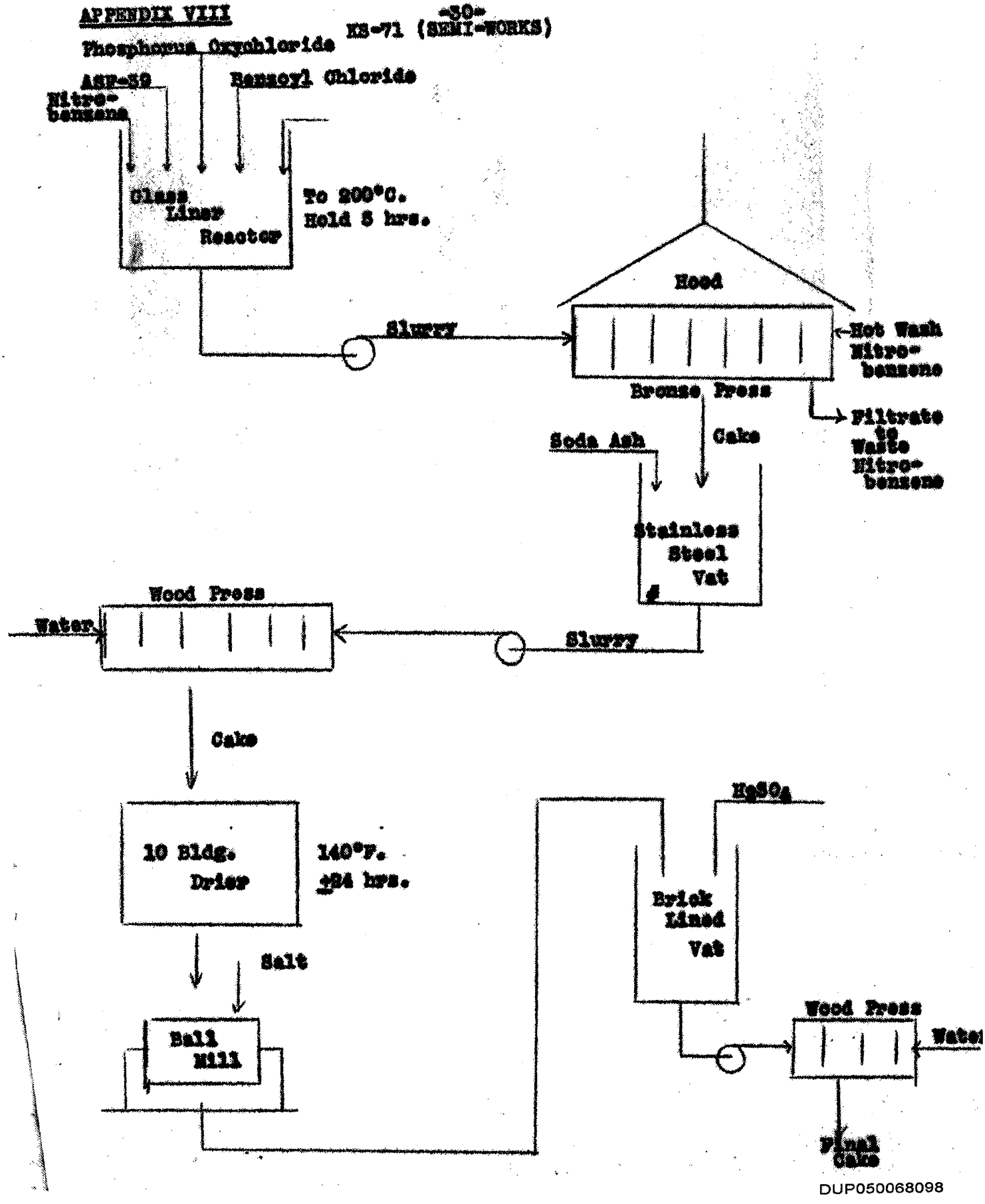
ASP-59 (SEMI-WORKS)

Chlorantil



APPENDIX VIII

KS-71 (SEMI-WORKS)



DUP050068098

APPENDIX IX

FORMULA CARD

COLOR CODE: DATE: FILE: 152-39 "Dianilide" Intermediate

OBJECT: Manufacture of K S-71 Violet Intermediate

BASED ON:

BATCH SIZE-MOLS: BATCH No. OF "K" BY-PASS:

GR. OR CONC.	MATERIAL	SYSTEM	GAL.	A. S.	MANIPULATION	HR.
					To 210 gallon vat add	
	Water		42			
					Add	
16# 6	oz. Sodium Acetate					
					Cook to solution at 105°F.	
					Add solution	
33#	13 oz. p-Anisic hydrazyl					
					Add dry	
24#	10 oz. Chloranil					
					Cook to 195°F.	
					Hold at 195°F. for 2 hours.	
					Filter hot.	
					Wash chloride free	
					Dry at 140°F.	

PACKAGE: LBS. PER: COST GROUP: SIGNATURE: F. F. EHRICH

GOAL YIELD: 53# 2 oz.

DUP050068099

FORMULA SHEET

COLOR CODE BT-711-D NAME Tentative Plant Process NAME ES-71 Dioxazine Violet Toner K

CHARGE Tentative Plant Process

BASED ON 1309-20

BATCH SIZE-MOLE 0.5 CHARGE No. OF "KT" CHARGES

LBS. OR GMS.	MATERIAL	MOLES	GAL.	C. C.	MANIPULATION	HR
					Charge to glass lined reactor (do not cool condenser) (Wear gas mask during handling	
245	Nitrobenzene (tech.)		24.5		of benzoyl chloride and phosphorus	
					oxychloride).	
76#	10-1/2 oz. ASF-29 (Lots					
	(294, 295					
17#	2 oz. Phosphorus oxychloride					
9# 5	1/2 oz. Benzoyl chloride					
					Seal reactor, start agitator.	
					Heat to 200°C and maintain at 200° ±3°C.	
					for 5 hours.	
					(Hydrogen chloride fumes are liberated).	
					Add to reactor from head tank	
61#	Nitrobenzene (tech.)		6.1		previously heated to 110°C	
					Cool charge to 100°C. (cold oil	
					circulation)	
					Pump to bronze filter press (hood)	
					(Orlon filter cloth) and wash with	
1225#	Nitrobenzene (tech.)		122.5		previously heated to 100°C., until	
					the filtrate shows a clear bright red	
					fluorescence.	
					(Reslurrying of filter cake may be	
					necessary. Filter cakes may be	
					tightened by blowing compressed nitrogen)	
					Check cake in lab. for completeness	
					of washing and for behavior on steam	
					distillation.	
					Transfer filter cake to steam still	
					Add	
	Water		120			
10#3	1/2 oz. Sodium Carbonate				Pass steam until nitrobenzene	3
					is completely removed.	
					Filter hot (wood press). wash free of	
					alkali. Dry at 180°F.	

PACKAGE LBS. PER COST OR. UP SIGNATURE F. F. EHRICH

GOAL YIELD 31# 9 oz.

DUP050068100

APPENDIX II

FORMULA SHEET

COLOR CODE BC-311-D DATE 5/7/49 NAME 23-71 Diazaine Violet K-

CHANGE Manufacture by "one-solvent process".

BASED ON 1309-62-B, 1309-47-B

BATCH SIZE-KGS. BATCH WT. 57 lbs. BARRELS

EQ. OF CHG.	MATERIAL	SPECIFIC	GAL.	C. F.	MANIPULATION	MS
					Charge to glass lined reactor provided with	
515	Nitrobenzene (tech.)		51.4		reflux condenser.	
62#	2 oz., Chloranil					
85#	5-1/2 oz. p-Aminobiphenyl (molten)					
					Seal reactor, start agitator	
					Heat to 100°C. and maintain at 100°C.	
					±5°C. for 4 hours	
					(HCl fumes are liberated)	
					Add to reactor (wear gas mask)	
28#	13 oz. Phosphorus oxychloride				Cave III	
15#	12 oz. Benzoyl Chloride					
					Heat to 200°C. and maintain at 200°C.	
					±3°C. for 5 hours.	
					(HCl fumes are liberated)	
					Dilute with nitrobenzene and pressed	
					as in standard formula.	

PACKAGE LBS. PER COST GROUP SIGNATURE F. F. EHRICH

GROSS WEIGHT 57 lbs.

DUP050068101