

Serial No.

Copy No.

KN-53-17

E. I. DU PONT DE NEMOURS & COMPANY
KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

"LITHOSOL" VIOLET 4RN - LAKES OF IMPROVED TEXTURE

MAY 1950 - OCTOBER 1950

Period Covered

A-IC-52

FILE:

DATE:

223.61

8/21/53

Serial No. KN-53-17

Copy No. /

COPY TO:

- #1 - Numerical File
- 2 - Research File (223.41)
- 3 - Library File (223.41)
- 4 - J. N. Tully/A. Siegel
- 5 - H. Arnoul
- 6 - J. H. Cooper
- 7 - F. F. Ehrich
- 8 - #14 Building File
- 9 - Extra
- 10 - Extra

NEWARK PLANT
PIGMENTS COLOR RESEARCH REPORT
FINAL REPORT

TITLE: "LITHOSOL" VIOLET 4RN - LAKES OF IMPROVED TEXTURE

CHARGE: A-IC-52

PERIOD COVERED: MAY 1950 - OCTOBER 1950

SUBMITTED BY: *F. F. Ehrich*
F. F. EHRICH

APPROVED BY: *J. H. Cooper*
J. H. COOPER

DATE SUBMITTED: 7/16/53

DATE ISSUED:

INTRODUCTION:

Work on improving BP-176-D was started specifically to meet the requirements of the Ford Motor Company. BP-176-D is an alumina hydrate lake of "Lithosol" Brilliant Violet 4RN containing ten percent of dye. This violet is used by Ford as a red toning agent and due to poor texture and dispersability, the desired strength level and degree of redness was not obtained within a reasonable alkyl grinding cycle. Whereas some of the difficulties associated with BP-176-D were due to quality variations in the "Lithosol" Violet 4RN dyestuff purchased from Orehem, the major problem centered about poor texture which could be attributed to aggregation of the acid-pasted dyestuff on drying. Furthermore, the texture problem was intensified by the Ford Motor Company rubout procedure for pigment evaluation, which involves mulling the pigment together with titanium dioxide and alkali refined Linseed oil under conditions which undoubtedly cause little work to be done on the pigment. In the course of this development, Harmon offered to the Ford Motor Company a violet lake (B-4000) which was decidedly superior to our BP-176-D offering.

Because of the urgency of the problem, the initial attempts to improve BP-176-D quality were made directly in the semi-works and in the plant.

Work on improving the texture and rate of strength development of BP-273-D was a direct outgrowth of the work done on the Ford Motor Company problem. The ammonium rosinate technique was found to be preferable to the sodium rosinate method for the purposes of texture improvement.

SUMMARY AND CONCLUSIONS:

BL-333-D lake prepared by extending a 50% "Ramapo" of "Lithosol" Violet 4RN (N-612) with blanc fixe to approximately 10% dye content was offered to and was accepted by the Ford Motor Company as satisfactory against Harmon's B-4000 counteroffering.

A BP-273-D(E) formula involving the use of ammonium rosinate in place of sodium rosinate has been developed and has been accepted by the plant for future production of this code. The product is decidedly superior in texture against the sodium rosinate counterpart.

DISCUSSION OF RESULTS:

Initial studies related specifically to the requirements of the Ford Motor Company were carried out directly in the plant, semi-works and laboratory and were concerned mainly with the following variations from the standard BP-176-D formula.

a. BP-176-D

Prepared in the semi-works draft tube unit with and without

the use of Goulac as a dispersing agent and extended with dry alumina hydrate. The products have a marked strength advantage over standard and over a product made by the standard formula from the same lot of dye. The rubout (standard method) strength advantage exhibited by the Goulac dispersed products over the undispersed products is not duplicated in an alkyl enamel system.

A 2000# batch of material prepared in the plant draft tube unit without the use of Goulac was s. red to red and 92:100 in strength against standard BP-176-D by the Ford rubout procedure.

b. ABP-328-D

Preparation of BP-273-D and extension thereof in slurry form with blanc fixe to the toner content of BP-176-D. Two batches prepared in the semi-works draft tube were red and strong against standard BP-176-D (standard rubout).

c. BBP-328-D

Reslurrying of BP-299-P (washed presscake of BP-273-D) and extension thereof in slurry form with dry blanc fixe. One 500 lb. plant batch prepared in the Abbe'-Lenart mixer was 90:100 s. int. and red vs. standard BP-176-D by the Ford rubout method.

d. ABP-331-D

Reslurrying of BP-299-P and extension thereof in slurry form with dry alumina hydrate. A semi-works draft tube batch was v.s. blue and strong vs. BP-176-D (standard rubout). Two 500 lb. batches were made in the plant Abbe'-Lenart mixer. Both proved red and strong by the Ford rubout method.

e. BBP-331-D

Preparation of BP-273-D and extension thereof in slurry form with alumina hydrate. A semi-works draft tube batch was red and strong against BP-176-D by both the Ford rubout method and by standard rubout procedure.

A 3800 lb. blend of several of the above products for shipment to Ford was prepared. The Control Laboratory described the product as being essentially equal in strength, v.s. red to red. and intense against standard BP-176-D by the Ford rubout method.

Attempts to recover substandard BP-176-D by reslurrying in the presence of wetting and dispersing agents have given marked improvement in strength and redness over the original. The most marked improvement was obtained by dispersing with Blancol and precipitating the Blancol as the barium salt. By the Ford test, the resulting product was equal in strength and v.s. blue against standard BP-176-D and s. strong and distinctly red against the original.

In general, it has been found that significant variation in strength and hue is possible for a given lot and for a given dye content, depending upon the manner of processing the product. Further, the Ford rubout method gives strength and hue readings which are in marked contrast with those obtained by the standard varnish drier rubout procedure and there are indications that strength shown by rubout, will not necessarily be realized in an alkyd grind.

Analysis of the Harmon counteroffering (B-4000) to our BP-176-D suggested the following composition:

77.45% Ba as BaSO₄
1.96% Al as Al₂O₃
9.90% Rosin
10.69% Toner (by difference)

This corresponds to a 50% "Ramapo" type of toner extended with barium sulfate to approximately 10% toner content.

BL-333-D

A series of rosinated lakes of the above type have been prepared by the ammonium rosinate and sodium rosinate methods. The products are very strong against standard by the Ford rubout method and compare favorably with the Harmon counterpart in strength although s. blue.

BL-333-D lake, prepared by extending a 50% "Ramapo" lake of "Lithosol" Violet 4RN (N-612) with blanc fixe to approximately 10% dye content closely approximates Harmon's counteroffering.

Evaluations of various experimental products including ABL-328-D, ABL-331-D, ABL-333-D and BP-176-D, utilizing the Ford rubout test, ink mill grinds in alkali-refined linseed oil, and grinds in alkyd revealed marked differences in rate of strength development despite small differences in texture as determined by grit ratings. The results indicate that BP-176-D made by standard formula is quite variable in this respect and that a product of the ABL-333-D type is one of the best in rate of strength development.

Two semi-works batches of ABL-333-D have been made. The first (lot 2364) made from Orchem, lot 17, dye was vs. strong and slightly red versus the initial Harmon offering to Ford. The second batch (lot 2366) made from lot 19 dye was somewhat weaker and bluer than both lot 2364 and the Harmon product. The results essentially confirm the previous quality reports on lot 19 dye and indicate that hue is dependent to a significant extent on the quality of the dye used.

Strength development series of ABL-333-D products in the Ford alkyd system confirm the superiority of this material over standard BP-176-D, which in turn is superior to most of the recent

production of the latter code.

There appears to be a significant relationship between the strength obtained by the Ford rubout test and the rate of strength development realized in practical alkyd grinds. This seems to be in order in view of the observation that the Ford rubout method affords little opportunity for work to be done on the pigment and consequently requires it to be of good texture in order that a given strength level be realized.

A 2000 lb. batch of ABL-333-D has been manufactured in the plant (lot 17798) and approved for shipment to Ford. The product was rated 102:100, s. blue, s. dull against the experimental semi-works sample lot 2369, (A 50/50 mix of lots 2364 and 3366 ABL-333-D).

The difference in quality was predicted on the basis of the lots of dye available for use (32.1% lot 17, 52.2% lot 18, 15.7% lot 19). The experimental sample consisted of 50% lot 17 (the best of recent Orchem shipments), and 50% lot 19.

Lot 17798 was superior by Ford rubout to the latest shipment of Harmon's lake (C/53681) against which it was rated 95:100, red, and intense.

"Lithosol" Violet 4RN toner recovered from substandard BP-176-D by acid extraction of the alumina hydrate has been converted to the BP-273-D and ABL-333-D lakes. The products appear weak by rubout. Evaluation of the BP-273-D lake in Dulux in an attempt to duplicate the F & F long grinding cycle in this medium (so as to get an indication of the inherent strength in this recovered pigment) indicates the material to be reactive compared to standard BP-273-D.

Three plant batches (2,000 lbs. each) of ABL-333-D were made using lots 20 and 21 of Orchem dye (N-612). Based on Ford rubout and Ford alkyd enamel evaluation, all three batches were satisfactory for shipment versus lot 17798, the first lot of plant manufacture, and which Ford has set up as a temporary standard.

A 200 pound blend of the first four plant batches of BL-333-D has been prepared and has been accepted as the standard.

Indanthrene Brilliant Violet 4RA

Three lots of General's Indanthrene Brilliant Violet 4RA presscake (chemical equivalent of DuPont's "Lithosol" Violet 4RN) were tested in the ABL-333-D formula and found to be uniformly unsatisfactory by the Ford rubout procedure. The products prepared from General's dyestuff were exceedingly weak versus their counterparts prepared from current DuPont dye (N-612).

BP-273-P

A 50% "Ramapo" lake of acid-pasted "Lithosol" Violet 4RN

(N-612) has been prepared (semi-works) for comparison texturewise versus a standard BP-273-D (72% "Ramapo" lake). The product is coded ABP-337-D.

The ink mill evaluation tabulated below indicates the extent of texture improvement versus standard BP-273-D obtained by the use of ammonium rosinate in place of sodium rosinate in the BP-273-D formula. In all cases, the rate of strength development was superior to that of standard BP-273-D.

Code	SW Lot #	Description	1T	3T	5T	7T
EBP-273-D	2417	72% dye-ammonium rosinate	7	7	7-1/2	7-1/2
ABP-337-D	2418	50% " " "	7-1/2	8	8	8
BP-273-D	-SD-90870	standard	1	6-1/2	6-1/4	6-3/4

Alkyd evaluations of BP-273-D lakes prepared by the ammonium rosinate process (EBP-273-D) and the standard sodium rosinate process indicate a higher initial consistency for the ammonium rosinate products, presumably due to a higher oil absorption. There is no significant evidence of greater reactivity in the ammonium rosinate products.

An F & F, Phila. evaluation of an experimental ammonium rosinate-type product (EBP-273-D, S.W. 2417) revealed no evidence of reactivity in paint; but the product was criticized on the basis of tinctorial properties.

Quality Control evaluations of the two types of lakes confirm our findings with respect to the inherent superiority of the ammonium rosinate material in alkyd enamel (slight redness, intensity, and strength) and by the varnish drier rubout procedure (up to 30% strength advantage). The superiority of the ammonium rosinate product in texture and rate of strength development by ink mill test has been previously reported. Recommendation has been made that all future production of this code be made using the (E)BP-273-D formula and that a new standard be set up.

EXPERIMENTAL DETAILS:

The work reported here is recorded in the following notebooks:

NB-1357
NB-1378

APPENDIX:

- (1) Ford Test for BP-176-D (BL-333-D)
(information from R.H.Pohl/G.W.Johnson 5/22/50)

0.05 gms. BP-176-D
0.5 " Alkali refined linseed oil
0.5 " R-610 TiO₂

Place on Hoover muller plate, mix in by hand with spatula.
Mull 10x50 with 150 lbs. - weight on muller. Mount on glass.

(2) (A)BL-333-D formula (attached)

(3) (E)BP-273-D formula (attached)

(4) BL-333-D formula (attached)

REFERENCES:

- (1) Exposure Program - Violet Lake, BL-333-D and BP-176-D, Ford Alkyd Tints, 2/12/50.
- (2) Letter L. F. Andrews to F. F. Ehrich, 6/9/50, Harmon B-4000 vs BP-176-D.
- (3) Letter L. F. Andrews to J. H. Cooper, 6/16/50, BP-176-D Ford Motor Co.
- (4) Letter F. F. Ehrich to J. H. Bailey, 8/22/50, Platinum Violet Lake BL-333-D(B).
- (5) Letter F. F. Ehrich to F. E. Bolton, 8/1/50, "Ponsol" Violet Lakes for Ford Motor Co. Oil Absorption.
- (6) Letter J. C. Nissen to F. E. Bolton, 9/15/50, Proposed New Standard, Platinum Violet Lake BL-333-D (lot 718, SD-718) and 9/19/50, Supplementary Report.
- (7) Letter F. F. Ehrich to H. Arnoul, 9/19/50, "Platinum" Violet BP-273-D.
- (8) Letter E. C. Botti to W. F. Spengeman, 9/26/50, Platinum Violet Exposure.
- (9) Letter F. F. Ehrich to H. Arnoul, 10/20/50 "Platinum Violet" (E)BP-273-D
- (10) Letter J. C. Nissen to F. E. Bolton, 2/14/51, Viscosity Tests-Platinum Violet Lake, BL-333-D, SD-718.

jc

CODE: BL-333-B (B) APPROVED BY: FFE 8/21/50
 GOAL: 2005# SIZE: NA 8/22/50
 DEMO V.A.: CWO 8/23/50
 COUPLING V.A.:
 STRIKE V.A.: 240 & 390
 Std. Hrs. 5.7 Non-Bleeding GW 9/26/50

VAT	NAME: PLATINUM VIOLET LAKE	INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS.
Prep. 1	1. Chop to 1/2" diameter or less, weigh and hold at Vat 313 for step 9		200	239	200
	2. Weigh and hold at Vat 362 for step 21		100	16	100
	3. Weigh and hold at Vat 390 for step 29		1600	65	1600
240 2	4. Pump or run into vat 240		1852	612	1852
	# Lot	# Lot			
	# Lot	# Lot			
	5. Wash in drums.				
	6. Adjust to 15" (663G.).				
	7. Start Vat 240 agitator.				
313 3	8. Run 9" (135G) water into vat 313.				
	9. Dump in N-239 prepared in Step 1.				
	10. Stir 3 minutes or longer				
	11. Weigh and pour in		67	122	67
	12. Stir 15 minutes				
	13. When step 12 stirring completed, adjust Vat 313 to 23" (345G.).				
	14. Heat to boil.				
	15. Stir 30-45 minutes at boil to stable white emulsion. Emulsion must remain milk white and not become transparent on cooling.				
	Test and Record: Stability				
	16. Test and Record: pH Normal 9.0-9.3.				
240 4	17. Run Vat 313 into Vat 240 at once thru 20 mesh screen.				
	18. Stir 60 minutes.				
362 5	19. Run 9" (108G) water into Vat 362				
	20. Turn on agitator and steam				
	21. Dump in N-16 weighed in Step 2				
	22. Adjust to 12" (156G) at 150-155°F				
	23. Stir until dissolved				
390-240 6	24. When step 18 stirring completed, strike Vat 362 at 150-155°F into vat 240 on the surface in 10-15 minutes.				
	25. Start circulation pump and vat 390 agitator at 2000 R.P.M.				
	26. Heat to 200-205°F in 25-30 minutes.				
	27. Hold at 200-205°F for 30 minutes while circulating Vat 240 thru draft tube maintaining Vat 390 level 16" from the top.				
	28. Shut off steam.				
	29. Add N-65 weighed in step 3 into vat 390 draft tube in 25-30 minutes.				
	30. Stir and circulate 60 minutes maintaining level 16" from top.				

CONTD ON PAGE 2.

CODE: _____	EX (A) BU-333-D	APPROVED BY: _____
GOAL: 2000#	SIZE: _____	LG: 6/12/50
DIEZO VAT: _____		FFE: 6/12/50
COUPLING VAT: _____		HA: 6/12/50
STRIKE VAT: 240 & 390		CWO: 6/13/50
Std. Hrs. _____	Non-bleeding	JA: 6/23/50

VAT	NAME:	INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS.
Prep 1		1. Chop to 1/2" diameter or less, weigh and hold at Vat 313 for step 8	200	239	200
		2. Weigh and hold at Vat 362 for step 20	100	16	100
		3. Weigh and hold at Vat 390 for step 28	1600	65	1600
240 2		4. Pump or run into Vat 240	1852	612	1852
	# Lot	# Lot			
	# Lot	# Lot			
		5. Wash in drums			
		6. Adjust to 15" (663G.)			
313 3		7. Run 9" (135G.) water into vat 313.			
		8. Dump in N-239 prepared in step 1.			
		9. Stir 3 minutes or longer.			
		10. Weigh and pour in	67	122	67
		11. Stir 15 minutes			
		12. When step 11 stirring completed, adjust Vat 313 to 23" (345G.)			
		13. Heat to boil.			
		14. Stir 30-45 minutes at boil to stable white emulsion: Emulsion must remain milk white and not become transparent on cooling. Test and Record: Stability			
		15. Test and Record: pH _____, Normal 9.0-9.3.			
240 4		16. Run Vat 313 into Vat 240 at once thru 20 mesh screen.			
		17. Stir 60 minutes.			
362 5		18. Run 9" (108G.) water into Vat 362			
		19. Turn on agitator and steam.			
		20. Dump in N-16 weighed in step 2			
		21. Adjust to 13" (156G.) at 150±15°F.			
		22. Stir until dissolved			
390-240 6		23. When step 17 stirring completed, strike vat 362 at 150-155°F into vat 240 on the surface in 10-15 minutes.			
		24. Start circulation pump and vat 390 agitator at 2000 R.P.M.			
		25. Heat to 200-205°F in 25-30 minutes.			
		26. Hold at 200-205°F for 30 minutes while circulating vat 240 thru draft tube maintaining vat 390 level 16" from the top.			
		27. Shut off steam			

CONT'D ON PAGE 2.

VAT	PAGE: 2	CODE: BL-333-D	LBS: 2000#	INSTRUCTIONS	USE LBS.	N-CODE	ACCT LBS.
	28.	Add N-65 weighed in step 3 into Vat 390 draft tube in 25-30 minutes.					
	29.	Stir and circulate 60 minutes maintaining level 16" from top	Record: Time Started				
			" Time Minutes				
		NOTE: If necessary small increments of water may be added in order that slurry will just flow thru the circulation pump and into vat 390.					
	30.	When step 29 completed, shut off circulation pump and vat 390 agitator.					
	31.	Drain vat 390 into vat 240.					
	32.	Wash in vat 390.					
	33.	Check and Record: _____	"				
	34.	Press with agitation.					
		TIME START	TIME FIN	OPTR			
		" "	" "	"			
		" "	" "	"			
		Circulate pigment slurry before addition of ammonium rosinate emulsion.					
		Use steam pump for circulation in draft tube.					
		Lot 17 - 594-2/4 lbs. = 32.1%					
		18 - 969 lbs. = 52.2%					
		19 - 288-1/4 lbs. = 15.7%					

JPL: 7/4/50

CODE: _____ Z: (E)BP-273-D
 GOAL: 450# SIZE: _____
 DIAZO VAT: _____
 COUPLING VAT: _____
 STRIKE VAT: 209,211
 Std. Hrs. 6.5 Non-Bleeding
 APPROVED BY: _____
 FFE: 6/26/50
 LG: 6/26/50
 BA: 6/26/50
 CWO: 6/27/50
 GL: 6/30/50

VAT	NAME: PLATINUM VIOLET	INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS.
Prep 1	1. Chop to 1/2" diameter or less, weigh and hold for step 6		121	239	121
	2. Weigh and hold at Vat 307 for step 18		61	16	61
S.V. 2	3. Pump or run into strike vat thru 20 mesh screen		3000	612	3000
	# Lot	# Lot			
	# Lot	# Lot			
	# Lot	# Lot			
	# Lot	# Lot			
	# Lot	# Lot			
	# Lot	# Lot			
	# Lot	# Lot			
	4. Adjust to 11" (4490.)				
313 3	5. Run 6" (900.) water into Vat 313.				
	6. Dump in N-239 prepared in step 1.				
	7. Stir 3 minutes or longer.				
	8. Weigh and pour in		41	122	41
	9. Stir 15 minutes				
	10. Adjust to 14" (2100.)				
	11. Heat to boil.				
	12. Stir 30-45 minutes at boil to a stable white emulsion. Emulsion must remain milk white and not become transparent on cooling. Test and Record: Stability				
	13. Test and Record: pH _____, Normal 9.0-9.3.				
S.V. 4	14. Run Vat 313 into strike vat at once thru 20 mesh screen.				
	15. Stir 60 minutes.				
307 5	16. Run 6" (750.) water into vat 307.				
	17. Turn on agitator and steam.				
	18. Dump in N-16 weighed in Step 2.				
	19. Adjust to 8" (960.) at 150-155°F.				
	20. Stir until dissolved.				
S.V. 6	21. After step 15 stirring completed, strike vat 307 at 150-155°F into strike vat on the surface in 10-15 minutes.				
	22. Heat to boil in 25-30 minutes.				
	23. Stir at boil 30 minutes.				
	24. Flood to 50" (18500.)				
	25. Press without agitation.				
	Time Start _____ Time Fin _____ Optr _____				
	_____	_____	_____		
	_____	_____	_____		
	_____	_____	_____		

CONT'D ON PAGE 2.

PROCESS: (E)BP-273-D DATE: RA: 6/26/50

MAKING AREA NOTES JPL: 7/4/50

EST. LOSS LBS.

REMARKS

PRESSING AREA INSTRUCTIONS

VAT

DATE

TIME

RELEASED BY

PRESS NO. 92

NO. OF Cakes 70

PRESS WITH out AGITATION

WASH TO chloride-free* OHMS

MAKE FIRST TEST AFTER HRS.

LOAD ON 2 cars

SPECIAL INSTRUCTIONS Non-bleeding

Soda Ash wash all equipment.

*Wash chloride free in presence

SAMPLES of rosin.

DELIVER TO

PRESSING AREA NOTES

DESCRIBE YOUR YIELD

RECOVERY CONDITIONS

EST. LOSS LBS.

Cakes USED

HOURS WASHED OHMS

DRYER CARS ACTUAL OR PULP CONTAINERS

NOTES ON SPECIAL INSTRUCTIONS

SAMPLED BY

RELEASED BY

DRYING AREA INSTRUCTIONS

TYPE L.V. H.V. HURRICANE

HOURS 42 28 42

TEMP. 140 140 140

LUMP CONTAINER See chart

SPECIAL INSTRUCTIONS Non-bleeding

SAMPLES

DELIVER TO

DRYING AREA NOTES

LUMP -- OK -- WET -- SALTS -- CONTAMINATED WITH

REMARKS

NO. DRYER CARS PULLED

LUMP WEIGHT

EST. LOSS LBS.

SAMPLED BY

RELEASED BY

GRINDING AREA INSTRUCTIONS

GRINDER NO. 7 L.S.P.

SPECIAL INSTRUCTIONS Non-bleeding

SAMPLES 2 envelopes & 1 pint can

DELIVER TO Control Laboratory

DO NOT MIX BEFORE SAMPLING

PACKAGING See chart

GRINDING AREA NOTES

LUMP -- OK -- WET -- SALTS -- CONTAMINATED WITH

REMARKS

EST. LOSS LBS.

REMARKS

SAMPLED BY

DATE MIXED

QUALITY REMARKS

LUMP WEIGHT CHECK