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MEMORANDUM REPORT NO. F-102

"MONASTRAL" BLUE
EFFECT OF DISPERSION TECHNIQUE AND USE OF NEW FLOCCULATION-RESISTANT PIGMENTS ON FORMULATING PROPERTIES IN "DUCO" AND "DULUX"

INTRODUCTION:

In "Duco", formulating utility of W-505, "Monastral" Blue dispersed by ball milling (standard factory dispersion technique prior to period covered by this report) is limited. Ball mill W-505 induces objectionable red streaking under the action of the buffing wheel when used in significant quantities, especially in metallics. As a result, blue metallics have been formulated on a considerably more expensive Indo Blue W-594 basis. Ball milled W-505 also exhibits a red "flop" or two-tone causing difficulties in matching some competitive color offerings.

B-614 (ethyl cellulose) must be used with all "Duco" colors formulated with ball mill W-505 to control flocculation. Addition of B-614 reduces tinting lacquer solids, lowers unpolished gloss slightly and increases length of required mixing time, all undesirable effects. Prior to adoption of B-614, complaints against light "Duco" colors containing W-505 attributed to flocculation were received; complaints resulted from increasing blue intensity in circulating systems or loss of color and actual visible flocculate formation upon temporary circulating system shutdown.

In view of these deficiencies of ball milled W-505, a research program was undertaken at Flint under Project F-10002 to improve the formulating utility of "Monastral" Blue in "Duco". Approaches studied involved upgrading of quality of dispersion of W-505 through "49 Process" or "RX" grinding and achievement of an improved property balance through adoption of new "Monastral" Blue pigment forms to replace W-505. In the latter case, new flocculation-resistant "Monastral" Blues(Pigments Department's BP-366-D, Ramapo Lake and BT-373-D toner: Orchem's "Monastral" Fast Blue BNF were considered the prime candidates. A Flint research objective was simultaneously established to determine if these flocculation-resistant pigments offered formulating advantages over W-505 in "Dulux".

SUMMARY AND CONCLUSIONS:

1. In "Duco", optimum "Monastral" blue formulating properties were achieved through use of the "49 Process" dispersion techniques. "49 Process" dispersion yielded substantial improvements over ball mill ground material in resistance to red streaking and in strength and moderate improvements in early gloss retention on exposure, unpolished gloss and flocculation resistance. (Table I).

2. Improvement in red streaking resistance gained by "49 Process" dispersion will permit formulation of much of the blue metallic color range on a "Monastral" Blue W-505 basis with a resultant improved cost picture due to reduced requirements for expensive Indo Blue, W-594. Improvements in flocculation resistance was not sufficient to allow elimination of B-614 from colors containing W-505.

3. The Pigments Department's new flocculation resistant resinated "Monastral" blue lake, BP-366-D, did not offer sufficient advantages over W-505 in either "Duco" or "Dulux" to compensate for its cost premium of $0.93 per pound of toner above the cost of W-505. (Tables II and III)

4. BT-373-D and "Monastral" Blue Fast BNF, flocculation resistant "Monastral" blue toners offered by the Pigments Department and Orchem, respectively, were of no interest in either "Duco" or "Dulux" because of hard pigment texture which created unusual dispersion problems and because of lack of important property advantages over W-505. (Tables II and III)

5. In "Dulux", replacement of W-785/W-630 by W-505/W-630 pigmentations in the formulation of light blue-greens reduced color drift in accelerated circulating system stability tests (Figure 1). In "Duco" formulation of this color range with either W-785 or W-505 yielded equivalent circulating system color drift(Figure 2).

ACTION TAKEN OR PROPOSED:

1. The Production Department has specified exclusive use of "49 Process" grinding for all future factory manufacture of "Monastral" blue "Duco" tinting (253-0505).

2. In "Duco", the "Monastral" blue tinting content permitted for formulating use without expectation of red streaking upon buffing has been increased from 15% to 20%.

3. The "Dulux" green formulating practices have been revised to permit "Monastral" blue/Ferrite formulation of light blue-green tints.

CONTINUING LABORATORY WORK:

Pertinent exposure series will be followed.

DISCUSSION OF RESULTS:

Effect of Dispersion Technique in "Duco":

The "49 Process" was found to be the optimum dispersion technique for "Monastral" blue pigments in "Duco" (Table I). Use of the "49 Process" in preference to the ball mill grinding technique gave improved resistance to red streaking under the buffing wheel in metallics, increased tinting strength, improved unpolished gloss and reduced flocculation and improved early gloss retention upon exposure (TX-5200). Tinting prepared using the RX (two roll mill) dispersion was superior to "49 Process" material in degree of freedom from red "flop" but was only equivalent to ball mill tinting in the other formulating properties under consideration. The rolls dispersion is considered dangerous and costly and formulating advantages gained by decreased red "flop" were small in comparison to those gained by improved streaking resistance and increased strength of the "49 Process" tinting.

Use of "49 Process" W-505 tinting (253-0505 now manufactured exclusively by the "49 Process") in combination with improved zinc oxide free Milori Blue, 253-0582, will significantly reduce costs of medium and dark blue "Duco" colors by replacing expensive Indo Blue, Chromium tetrahydroxide blends required by past formulating practices to gain adequate streaking resistance.(Refer Release Letter F-522)

Flocculation-Resistant "Monastral" Blue Pigments in "Duco":

A comparison of formulating properties of W-505 and new flocculation-resistant "Monastral" pigments offered by the Pigments Department and Orchem is presented on Table II. Laboratory "49 Process" "Monastral" dispersions were compared for all properties except color drift in circulating systems; here plant ground W-505 served as the control.

The present forms of BT-373-D and Orchem's BNF were of no interest because of hard pigment texture. "49 Process" dispersions of both pigments were extremely gritty. Grit could be eliminated by ball mill or slurry grinding but streaking resistance and strength of such dispersions were inferior to even the gritty "49 Process" tinting. The Pigments Department recognizes the deficiencies of BT-373-D and expects to introduce a flocculation-resistant toner having improved texture and strength in about one year.

BP-366-D was the most promising of the flocculation-resistant pigments investigated (Table II). It offered a definite improvement over W-505 in resistance to red streaking under the buffing wheel in metallics, exhibited less red "flop" and generally better metallic two-tone than W-505 and was superior to W-505 in inherent flocculation-resistance. Light blue-green tints (Nile Green) formulated with BP-366-D without B-614 showed less color drift in a circulating system than matching W-505 formulations with B-614. (Table IV and Figure 2). However, BP-366-D was 15% weaker in tinting strength than W-505 on an equal toner basis and sells for a cost premium of $0.93per pound of toner over W-505. Except for small differences in gloss retention, durability of "49 Process" dispersions of both pigments were equal upon four months Florida exposure (TX-5200).

Analyzing each advantage offered by BP-366-D, the following was observed: The improvements in red streaking and red "flop" gained by use of BP-366-D are, of course, desirable. However, upgrading of streaking-resistance of W-505 achieved by adoption of the "49 Process" dispersion technique will permit a very substantial expansion of the area usage of "Monastral" blue in "Duco". The additional reduction in streaking gained by use of BP-366-D may not have commercial significance. The limiting effect of red "flop" on the use of W-505 only applies to a relatively few colors. No significant complaints have been received against W-505 containing colors relating either to flocculate formation or to color drift in circulating systems since the initiation of the use of B-614, therefore, the improved inherent flocculation-resistance of BP-366-D does not appear to be required at the present time. Use of BP-366-D would permit elimination of B-614 in the formulation of "Monastral" blue with a consequent slight improvement in gloss, higher solids and reduced mixer cycle. These latter improvements, while desirable, are small in comparison to the cost premium commanded by BP-366-D.

To conclude, under present "Duco" formulating requirements the advantages offered by BP-366-D do not appear of sufficient value to compensate for its high pigment cost and strength deficiency. We do not propose adoption of BP-366-D in "Duco" at this time.

Flocculation-Resistant "Monastral" Blue Pigments in "Dulux":

BT-373-D and Orchem's BNF offered advantages in metallic red "flop" over W-505 at the expense of reduced tinting strength. Low tinting strength of these two pigments appeared to be due to grinding difficulties induced by hard pigment texture (Table III).

BP-366-D yielded only higher grinding solids, improved grinding consistency and less metallic red "flop" (as compared to W-505) to compensate for higher pigment cost at equal strength (Table III). BP-366-D was superior to W-505 in flocculation-resistance by pour, storage and rubout tests. However, this improvement is not presently required since no significant complaints due to flocculation of W-505 colors have been received. No improvements in circulating system color stabilitycould be demonstrated for BP-366-D over W-505 in "Dulux" (Table IV and Figure 1). Exposure Series TX-5277 has been prepared to determine comparative durability of W-505, BP-366-D, BT-373-D and BNF. Four month Florida exposure results will be available in January 1954.

Formulation of Light Blue-Green Tints:

"Dulux":

Circulating system color drift of Nile Green(typical blue-green tint) was substantially reduced by formulation with W-505/W-630 combinations in place of W-785/W-630 pigmentations required by past formulating practices. (Table IV, Figure 1).

"Duco":

Nile Green formulated with either W-505/W-630 or W-785/W-630 pigmentations exhibited equal circulating system color drift. (Table V, Figure 2)

EXPERIMENTAL DETAIL:

Test Methods:

A. Color:

Hue and brightness were compared visually from sprayouts over 4" x 6" cardboard panels in the case of white tints and from sprayouts over undercoated 4" x 12" Bonderite panels in the case of metallics.

B. Tinting Strength:

Strength was obtained by means of a graphical comparison of colorimetrically (Colormaster) determined lightness values of 95/5 (pigment ratio) tints of white and the "Monastral" dispersion under consideration. "49 Process" dispersed W-505 was selected as control and assigned the strength of 100%.

C. Two-Tone and Red "Flop":

Metallic Two-tone and red "flop" were determined by visual comparison of sprayouts over undercoated 4" x 12" Bonderite panels.

D. Flocculation:

Three tests measuring degree of flocculate formation of "Monastral" dispersions were utilized. These tests were considered indicative of flocculation difficulties that would be encountered commercially upon temporary shutdown of a circulating system. The tests were performed using 95/5 (pigment) white/"Monastral" tints.

1. Pour-out test:

A color card was sprayed as soon as possible after preparation of the tint. Pour-outs of the same tint were then made over the sprayed card initially and after one, two and four hours unagitated storage. In the case of "Duco", material to be poured was thinned to yield a consistency half-way between package and spray viscosity. "Dulux" was poured at package viscosity. Apparent loss of strength of the pour indicated flocculation. The difference in lightness between pour and sprayed background was considered to be a measure of the degree of flocculation. Visual comparisons were made in collecting the data presented on Table I. The ratio of the colorimetrically determined lightness of the pour to lightness of the color card is presented on Tables II and III.

2. Storage:

The tint was thinned to spray viscosity and stored in a glass container. Flocculation showed up as uneven agglomerates of pigment on the walls of the bottle. Both the storage and pour tests for flocculation were modeled after testing method #602, "Evaluation of Automotive and Refinish "Duco", Testing Methods, Parlin Laboratory".

3. Rub Test:

This test, limited to "Dulux", consisted of rubbing the freshly sprayed film just prior to set-up. If significant blue flocculation had occurred since sprayout, rubbing broke down the flocculates resulting in an increase in blue intensity of the rubbed area as compared to the unrubbed area.

E. Circulating System Color Drift:

Matches to Nile Green (246-55879 - blue-green tint) were prepared using combinations W-63, and the "Monastral" dispersions specified in Tables IV and V with white and black (if required). In the case of "Duco", 5% B-614 (based on tinting) was added to all matches except the one formulated using BP-366-D. These paints were aged 10 days at package viscosity, mixed by spatula, reduced to spray viscosity and charged into a laboratory gallon porcelain crock with stone pebbles at a 40/80 grinding ratio. Samples were taken from the mills after the specified grinding times. Triplicate independent sprayouts of each sample over cardboard were prepared. Each panel was colorimetrically analyzed in the following manner: Colormaster "G", "R" and "B" values were measured according to the absolute method of operation of the Colormaster described in Engineering Department Report DED-X-52-44. "G", "R" and "B" were utilized to calculate tri-stimulus values, X, Y and Z, by the relations specified in DED-X-52-44. The trichromatic coefficients, x, and y, were then calculated from the tristimulus data. The arithmetic averages of the Y (lightness), the x and the y values of the triplicate sprayouts of each sample are presented in Table IV and V. This data was graphically analyzed as C.I.E. plots on figures 1, 2 and 3. The diameter of the circles on these figures was selected to represent approximate confidence limits for the determinations.

In this experiment, circulating system attrition was simulated by pebble mill grinding to save time and material. Figure 3 shows that color drift upon pebble mill grinding followed the same curve as drift in a five gallon model of the type circulating system used commercially.

Nile Green was selected for study because it was considered representative of the type of color, formulated with "Monastral" blue, most subject to color drift difficulties.

F. <u>Red Streaking:</u>

Red streaking under action of the buffing wheel in "Duco" was determined for Trophy Blue (281-55656 - 11/22/50) metallics formulated using the "Monastral" dispersions under consideration. Sprayouts over 12" x 26" undercoated panels, baked 29' x 180°F. were prepared for testing. Film thickness was held at 2.0 ± 0.2 mils. The streaking test consisted of buffing the panel in the normal manner followed by buffing with the edge of the wheel. In the second buff, the wheel was applied on edge at the top of the panel under light pressure; as the wheel was brought down the panel pressure was increased gradually until sufficient pressure was applied near the bottom of the panel to burn into the film. Several passes with the edge of the wheel were made for each panel. Red streaking showed up as a red smear along the area hit with the edge of the buffing wheel. Severity of red streaking of comparative compositions was rated visually.

Trophy Blue was selected as test color since customer complaints of red streaking against Trophy Blue as formulated with ball mill W-505 caused virtual elimination of W-505 from blue metallic formulations.

FLINT LABORATORY

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TABLE I
"MONASTRAL" BLUE
EFFECT OF DISPERSION TECHNIQUE IN "DUCO"

Pigment	Tinting Code	Dispersion Method	Masstone Gloss Init. Unpol. 60°	Masstone Gloss 4 Mo. Exp.(1) 20°ASTM	Tinting Strength (2)	Flocculation(3) With 5% B-614	Flocculation(3) Without B-614	Red Streak-ing(4)	Red Flop (5)
W-505	F-253-N-5053	Lab Ball Mill	77°	53°	85%	8	3	1	5
	F-253-N-5012	Lab 49 Process	85°	92°	100%	9	6	6	4
	253-059 F-4624595	Plant Ball Mill	-	-	-	--	-	1	4
	J-253-X-011923 J-456372	Plant 49 Process	-	-	-	-	-	5	4
	F-253-X-5077	Lab RX	87°	85°	86%	-	4	2	7
BP-366-D	F-253-N-5055	Lab Ball Mill	70°	30°	71%	10	10	6	-
	F-253-N-5014	Lab 49 Process	85°	65°	85%	10	8	8	9
W-525 (BT-297-D)	F-253-N-5054	Lab Ball Mill	62°	25°	62%	8	3	-	-
	F-253-N-5013	Lab 49 Process	80°	66°	69%	8	6	3	-
BT-282-D	F-253-N-5056	Lab Ball Mill	34°	17°	82%	10	8	-	-
	F-253-N-5015	Lab 49 Process	77°	76°	89%	10	10	8	8

(1) 20° ASTM gloss of masstone panels following four months Florida exposure in Series TX-5200. Panels were washed. Buffed gloss of all panels prior to exposure was equal.
(2) Determined in white tint (95/5 - W-50/Monastral toner) from lightness valuesmeasured using the Colormaster (DuPont Differential Colorimeter).
(3) Determined from pour-out test in white tint (95/5 - W-50/Monastral toner); flocculation considered proportional to color difference between initially sprayed color card and pour-out after four hours undisturbed storage.
(4) Red streaking under action of buffing wheel in Monastral formulation of Trophy Blue, 281-55656 dated 11/22/50.
(5) Red "flop" or two-tone in Monastral formulation of Trophy Blue.

Numerical rating: 10 = None; 5 = Moderate; 1 = Severe.

TABLE II
NEW FLOCCULATION-RESISTANT "MONASTRAL" BLUE PIGMENTS IN "DUCO"
"49 PROCESS" DISPERSIONS

System	Code	Property	Pigme		
			W-505 Control	BP-366-D	I
Masstone	W-505 : F-253-N-7056 BP-366-D : F-253-X-7117 BT-373-D : F-253-N-7016 BNF : F-253-N-5078	Unpol.60° Gloss Grit Solids Brookfield 20RPM Viscosity 10RPM 4RPM	85 Grit Free 34.4% 3100 cp 4500 7500	85 Grit Free 33.4% 1200 cp 1200 1250	 W
White Tint W-50/Monastral toner - 95/5 Without B-614	W-505 : F-253-N-7023 BP-366-D : F-253-N-7024 BT-363-D : F-253-N-7025 BNF : F-253-N-5078	Tinting Strength Color: Hue Brightness Flocculation: Pour-out test(1) Storage 72 Hr(2)	100% Control Control 1.06 1	85% Green Dull 1.01 10	 F S
Metallic Monastral toner/ W-94 - 90/10	W-505 : F-281-N-7026 BP-366-D : F-281-N-7027 BT-373-D : F-281-N-7028 BNF : F-281-N-5095	Hue (head on) Two-Tone Red "Flop"	Control Control 4	Green & Dull Greater 6	F I
Trophy Blue 281-55656 dated 11/22/50	W-505 : F-281-N-7039 BP-366-D : F-281-N-7040 BT-373-D- : F-281-N-7041 BNF : F-281-N-5095	Red Streaking Under Buffing Wheel	5	8	
Nile Green	W-505 : F-253-N-7108 BP-366-D : F-253-N-7010	Color change in simulated circulating system	Control (With B-614) See Table IV & Fig. 2	1/3 W-505 change (without B-614)	
Pigment Cost per pound of toner:			$ 3.85	$ 4.78	$

(1) Ratio of lightness of pour after 4 hours undisturbed storage to lightness of in
card.
(2) Material stored undisturbed in glass container; presence of blue flocculates on
container noted after 72 hours.
Numerical ratings: 10 = None; 5 = Moderate; 1 = Severe.

TABLE III

NEW FLOCCULATION RESISTANT "MONASTRAL" BLUE PIGMENTS IN "DULU

"47 PROCESS" DISPERSIONS

System	Code	Property	P i g	
			W-505 Control	BP-366-D
Mill Base	W-505 : F-42-N-7069 BP-366-D : F-42-N-7067 BT-373-D : F-42-N-7072 BNF : F-42-N-7074	Grit Solids Brookfield Visc: Init: 20 RPM 10 RPM 2 Mo: 20 RPM 10 RPM	Grit Free 27% 780 cp 1460 718 1360	Grit Free 39% 325 cp 440 420 440
Tinting Enamel	W-505 : F-92-N-7070 BP-366-D : F-92-N-7071 BT-373-D : F-92-N-7073 BNF : F-92-N-7075	Masstone Gloss 60°	90°	91°
White Tint M-43/Monastral Toner - 95/5	W-505 : F-92-N-7020 BP-366-D : F-92-N-7021 BT-373-D : F-92-N-7022 BNF : F-92-N-7103	Tinting Strength Color: Hue Brightness Flocculation: Pour-out test(1) Storage (2) Rub-out (3)	100% Control Control 1.01 1 Strong	100% Equal V.Sl.Dull 0.96 9 Weak
Metallic Monastral toner/ W-94 = 90/10	W-505 : F-192-N-7029 BP-366-D : F-192-N-7030 BT-373-D : F-192-N-7031 BNF : F-192-N-7107	Hue (Head on) Brightness Two-Tone Red "Flop"	Control Control Control 6	Green Equal Equal 10
Nile Green	W-505 : F-92-N-5124 BP-366-D : F-92-N-5125 BT-373-D : F-92-N-7017	Color change in simulated circulating system	Control	No advanta W-505. S and Figur
Pigment Cost per pound of toner			\$ 3.85	\$ 4.78

(1) Ratio of lightness of pour after 4 hours undisturbed storage to lightness of color card.

(2) Material stored undisturbed in glass container; presence of blue flocculates of container noted after 72 hours.

(3) Apparent strength of area of color card rubbed just prior to set-up of the en with strength of unrubbed areas.

Numerical Rating: 10 = None; 5 = Moderate; 1 = Severe.

TABLE IV

"DULUX" COLOR DRIFT OF "MONASTRALS" UNDER CIRCULATING SYSTEM ATTRITION
APPROXIMATE MATCHES TO NILE GREEN

Code	"Monastral" Pigment	"Monastral" Dispersion Method	Time of Circulation	Y	x	y
F-92-N-5124	W-505	Lab. 47 Process	Initial	24.45	0.2658	0.3226
			24 hr.	24.57	0.2659	0.3228
			48 hr.	24.74	0.2651	0.3229
			96 hr.	24.81	0.2644	0.3225
			12 day	24.79	0.2625	0.3218
F-92-N-5125	BP-366-D	Lab. 47 Process	Initial	24.29	0.2659	0.3235
			24 hr.	24.45	0.2655	0.3242
			48 hr.	24.67	0.2652	0.3239
			96 hr.	24.71	0.2635	0.3234
			12 day	24.64	0.2616	0.3224
F-92-N-7017	BT-373-D	Lab. 47 Process	Initial	24.73	0.2682	0.3259
			24 hr.	24.95	0.2687	0.3276
			48 hr.	25.16	0.2683	0.3272
			96 hr.	25.50	0.2682	0.3273
			12 day	26.04	0.2674	0.3271
F-92-N-5123	W-785	Lab. 47 Process	Initial	24.87	0.2711	0.3287
			24 hr.	24.52	0.2715	0.3279
			48 hr.	24.28	0.2713	0.3271
			96 hr.	23.84	0.2706	0.3260
			12 day	23.07	0.2698	0.3232

TABLE V

"DUCO" COLOR DRIFT OF "MONASTRALS" UNDER CIRCULATING SYSTEM ATTRITIO
APPROXIMATE MATCHES TO NILE GREEN

Code	Monastral		B-614 Content	Source of Circulating Action	Time of Circulation	60° Gloss	Y
	Pigment	Dispersion Method					
F-253-N-7108	W-505	Plant 49 Process	5%	Rotation in Pebble Mill	Initial 24 hr. 48 hr. 96 hr. 12 day	78 73 80 82 87	23. 23. 23. 23. 24.
F-253-N-7010	BP-366-D	Lab. 49 Process	0%	Rotation in Pebble Mill	Initial 24 hr. 48 hr. 96 hr. 12 day	77 78 78 80 80	24. 24. 24. 25. 25.
F-253-N-7110	W-785	Plant VX Process	5%	Rotation in Pebble Mill	Initial 24 hr. 48 hr. 96 hr. 12 day	80 80 81 81 88	25. 25. 26. 26. 26.
F-253-N-7108	W-505	Plant 49 Process	5%	Passage Through Small Scale Circulating System	Initial 1 hr. 2 hr. 11 hr. 24 hr.	78 80 80 80 74	23. 23. 23. 23. 23.

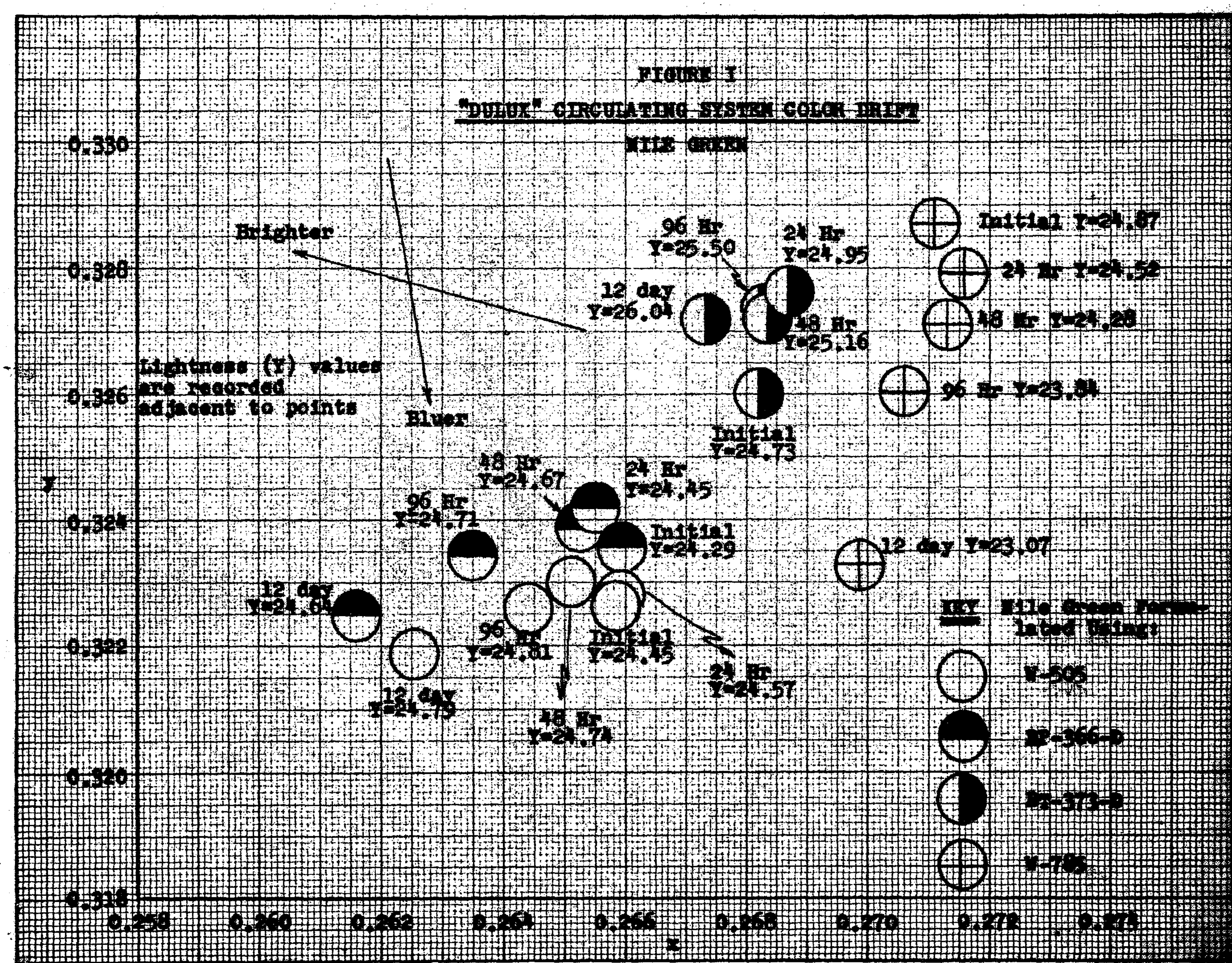

FIGURE I
"DULUX" CIRCULATING SYSTEM COLOR DRIFT
NILE GREEN

FIGURE 2

"DUCO" CIRCULATING SYSTEM COLOR DRIFT

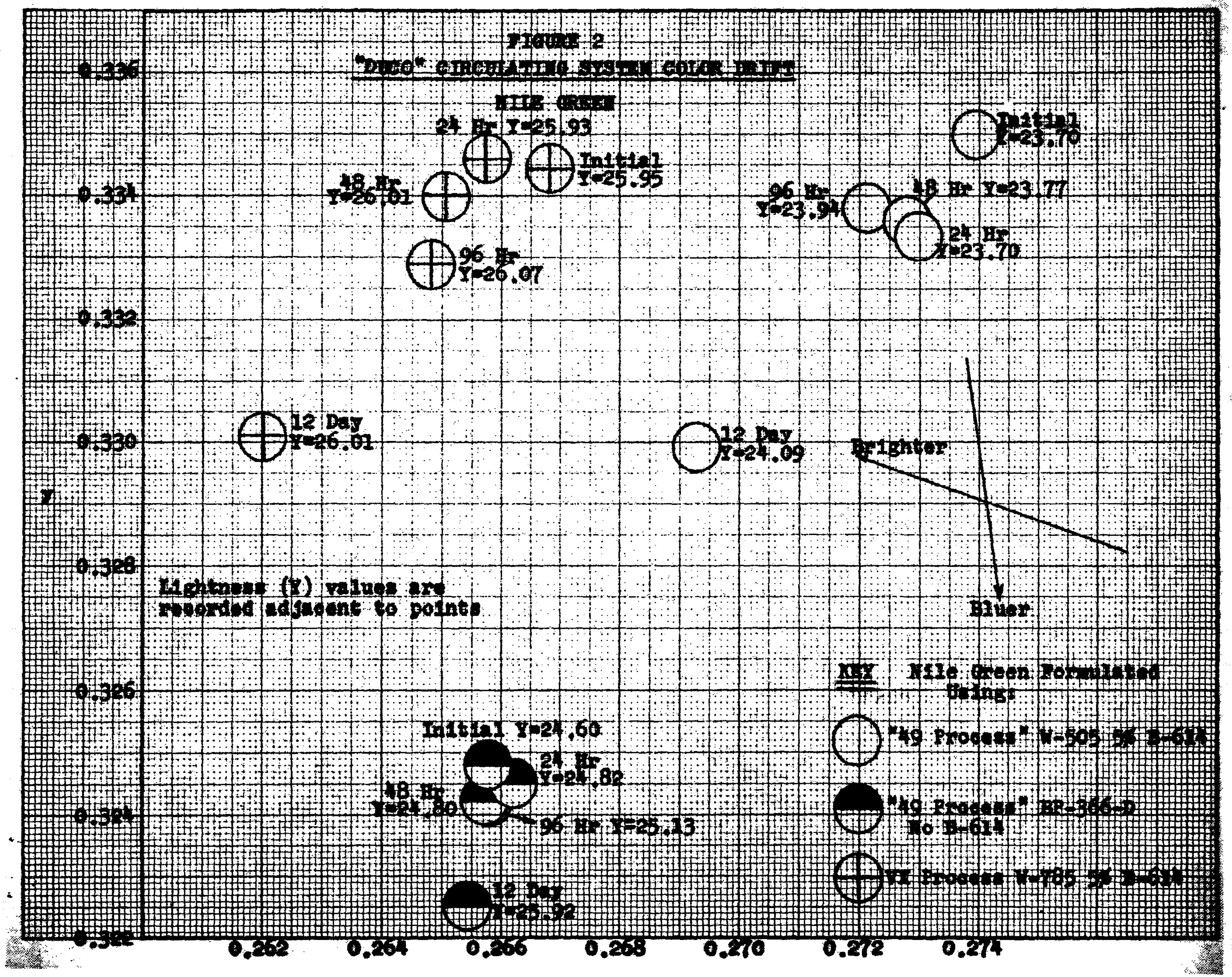

FIGURE 3

EFFECT OF METHOD OF APPLYING ATTRITION ON CIRCULATING SYSTEM COLOR DRIFT

NILE GREEN FORMULATED USING "49 PROCESS" W-505