C-1

cc: Mr. J. B. Bullitt, Wilmington
Mr. R. B. Davis, Marshall Lab
Mr. J. D. Pickens, Flint
Mr. R. E. Pike, "
Mr. T. R. Matthews, "
Mr. W. P. Kingsley, "
Mr. R. J. Fulmer, "

File: 1810

Flint 2, Michigan
May 25, 1953

CONFIDENTIAL

MEMORANDUM REPORT NO. F-93

PRELIMINARY EVALUATION OF CHROMIUM HYDROXIDE IN "DUCO" AND "DULUX"

INTRODUCTION:

Chromium Hydroxide (GI-734-D) is a pale green transparent extender pigment currently under development by the Pigments Department. It is considerably more transparent than chromium tetrahydroxide (W-701) but is not as colorless as Polymer K (nickel hydroxide). Chromium hydroxide has been examined for possible utility in the formulation of bright metallics.

In "Duco" metallics, it has been considered principally as:

1. A replacement for chromium tetrahydroxide (W-701) to upgrade exterior durability.

2. A replacement for clear base to upgrade exterior durability and/or working properties.

In "Dulux" metallics, chromium hydroxide is being considered as a possible substitute for Polymer K to improve durability of low P/B formulations.

This report summarizes the results and present status of the evaluation and development of chromium hydroxide in both "Duco" and "Dulux". The lots of chromium hydroxide pigment investigated are referred to by designations, defined in Table I, that are descriptive of the reaction used to prepare the pigment.

SUMMARY AND CONCLUSIONS:

"Duco"

1. "Duco" tinting lacquer formulated from "chloride" process chromium hydroxide pigment was superior in color and film integrity upon exposure in masstone to tinting formulated from "sulfate" process pigment. However, even the "chloride" tinting

checked severely on exposure in masstone, being inferior to Polymer K in this respect after one year in Florida (Table II).

2. Formulation of "Duco" metallics using either "chloride" or "sulfate" process chromium hydroxide pigment offered no durability advantages over controls prepared on existing practices.

A. Formulations prepared using "sulfate" process chromium hydroxide were inferior to matches based on Polymer K, Argent Gray or complementary blending in film integrity and/or polish back at twelve months Florida exposure (Table II).

B. Formulations based on chromium hydroxide (either "sulfate" or "chloride" process pigment) were intermediate in gloss retention, polish back or film integrity between matches prepared using a W-701 pigmentation (best) and by extension of a W-785 pigmentation with clear base to equal hiding (Table III). No significant advantages in blister resistance over W-701 could be demonstrated for either chromium hydroxide pigment in "Duco" lacquers on either one year Florida exposure (Table III) or by accelerated tests over a body undercoat (Table V).

3. Working properties of bright metallics were not improved by replacing clear base with chromium hydroxide (Table VI).

4. Package stability of chromium hydroxide in "Duco" was excellent (Table VII).

"Dulux"

1. The only durability background available to date involves "sulfate" process dry pigment ball milled or flushed in a "Dulux" vehicle system. The results of these exposures showed:

A. Ball mill dispersions of the dry pigment were superior in blister resistance on exposure to the flushed samples prepared by the Pigments Department (Table IV). No advantage in initial color was shown by the flushed sample.

B. In masstone, at optimum P/B ratio (15/100), "Sulfate" process pigment ball milled gave durability after eight months Florida exposure intermediate between Polymer K and chromium tetrahydroxide, W-701. It showed blister resistance superior to W-701 and no evidence of checking. It was inferior to Polymer K in gloss retention. (Table IV)

2. "Dulux" enamels formulated with plant or semi-works production lots of either "sulfate" or "modified chloride" process pigments showed satisfactory viscosity stability and freedom from settling after two months shelf storage. However, mill bases

formulated from the "modified chloride" process pigment bodied severely after two weeks at 110°F and showed surface livering after two months shelf storage. Mill bases of "sulfate" process pigment were satisfactory.

ACTION TAKEN OR PROPOSED:

1. Further evaluation of chromium hydroxide in "Duco" has been discontinued in view of lack of durability or working property advantages over existing practices. Surveillance of panels now on exposure is the only action proposed in "Duco".

2. In "Dulux", preliminary exposures of chromium hydroxide have yielded encouraging, but limited, durability results for the ball mill dispersion. Further development in "Dulux" will be delayed pending return of extensive exposures of ball mill dispersions of plant and semi-works scale "sulfate" process and semi-works scale "modified chloride" process pigment. Should these exposures continue to show durability advantages for chromium hydroxide over existing metallic formulating practices; the preferred pigment process will be selected, the cost picture will be developed and plant alignment undertaken in preparation for release of the ball mill dispersion of chromium hydroxide in "Dulux".

EXPERIMENTAL DETAILS:

Pigment Samples - The samples of chromium hydroxide received from the Pigments Department and the process reactions involved are listed in Table I. "Sulfate" process pigment was preferred by the Pigments Department on the basis of ease of manufacture. The"modified sulfate" process was a commercially impractical variation of the sulfate reaction. The "chloride" process was not considered desirable for large scale production because of the corrosive free chlorine by-product. Evaluation of free chlorine in the chloride process was eliminated in the "modified chloride" process by the introduction of formaldehyde as a reactent. The two samples of "modified chloride" process pigment differed only in that lot 1579 was heat developed while lot 1578 was cold struck. "Chloride" and "modified chloride" pigment will be more expensive than "sulfate" process pigment according to Pigments Department estimates.

Durability - Significant Florida durability results for exposures of experimental scale "sulfate", "modified sulfate" and "chloride" process chromium hydroxide pigment in "Duco" are presented in Tables II and III. Table II lists results comparing the experimental process samples with other transparent extenders in masstone and a bright metallic. Table III illustrates the effect on Florida durability of the replacement of W-701 or clear base by chromium hydroxide in bright "Duco" metallics. Four months Florida exposure results for plant and semi-works production lots of chromium hydroxide in "Duco" will be available 7/15/53.

Durability results in "Dulux" masstone of plant scale "sulfate" process chromium hydroxide are presented on Table IV. Four months Florida exposures of semi-works "sulfate" and "modified chloride" process chromium hydroxide in "Dulux" will be available 8/15/53.

Pigment Dispersion and Initial Properties - In "Duco" a pulp process PX dispersion was used. Attempts to utilize a dry pigment modified pulp process were unsuccessful because of excessive grit and poor color. "Dulux" dispersions were prepared by ball mill grinding.

In "Duco" lacquers, clarity (on flowout) of experimental scale "chloride" process pigment was superior to all other lots. Experimental "sulfate" process pigment was cloudy. The plant and semi-works pigments were equal in clarity, being intermediate in this respect between experimental "chloride" process and experimental "sulfate" process pigment. No differences were noted between flowout clarity of chromium hydroxide pigment samples evaluated in "Dulux".

Accelerated blistering results are tabulated on Table V for plant and semi-works production of chromium hydroxide in unexposed "Dulux" and "Duco" masstones, and for panels of "Duco" exposure series TX-5147 after one months Florida exposure. Accelerated blistering results on these pigments in "Dulux" after one month Florida exposure (series TX-5193) will be available 6/15/53.

The accelerated blistering test consisted of immersing the panels in distilled water at 98°F for a period of one week. The panels were periodically examined to note the time of initial blistering as well as the severity of blistering at one week. A body undercoat system was used ("Duco", 475-1195 primer; 683-1717 surfacer - "Dulux": 765-1676 primer-surfacer).

The effect on "Duco" working properties of the replacement of clear base by chromium hydroxide in a bright high aluminum content metallic is presented on Table VI. Hiding was measured by cryptometer. Scaling, mottling and patching where determined by spraying, buffing and patching 12" x 36" panels in the laboratory. The effect of chromium hydroxide on "Dulux" working properties was not determined.

Package Stability - Viscosity stability (two weeks 110°F and also two months shelf storage) and settling results (two months shelf storage) for plant and semi-works lots of chromium hydroxide in "Duco" and "Dulux" are presented on Table VII. Viscosities were measured by a Brookfield viscosimeter; averages of reading at spindle speeds of 10 and 20 rpm are recorded. Samples were stored in 3/4 full closed cans. Degree of settling was determined by applying a tapered spatula perpendicularly to the pigment cake.

FLINT LABORATORY

R. J. Fulmer

R. J. Fulmer

REP

TABLE I

TABULATION OF CHROMIUM HYDROXIDE SAMPLES RECEIVED FROM THE PIGMENTS DEPARTMENT

Pigments Dept. Code	Lot Number	State	Production Scale	Date Submitted	Process Reaction
1415-29-A	--	Pulp	Experimental	12/21/51	(A) Sodium chromate + hydrochloric acid yields ch chloride + chlorine gas + water. (B) Chromic chloride ppt to yield chromium hydrox
1415-29-C	--	Pulp	Experimental	12/21/51	(A) Sodium chromate + sodium bi-sulfate yields ch sulfate + sodium sulfate + water. (B) Chromic sulfate ppt to yield chromium hydroxi
1389-70 A	--	Pulp	Experimental	12/21/41	Modification of Sulfate Process
AGI-734-D	37226	Pulp	Plant	3/10/52	Same as 1415-29-C
	37226	Flushed in alkyd resin			
	37261	Dry			
AGI-734-D	1576	Pulp & Dry	Semi-works	11/13/52	Same as 1415-29-C
BGI-734-D	1578	Pulp & Dry	Semi-works	11/13/52	Evolution of chloride gas in 1415-29-A reaction by addition of formaldehyde as reactant.
BGI-734-D	1579	Pulp & Dry	Semi-works	11/13/52	Reaction same as for BGI-734-D Lot 1578. Pigmen developed.

TABLE II

COMPARISON OF FLORIDA DURABILITY OF CHROMIUM HYDROXIDE WITH OTHER EXTENDER PIGMENTS IN "DU

Pigment	Process	Exposure Series	In Masstone*					Color Matches to One		
			Exposed Gloss		Film Integrity			Exposed Gloss		Film I
			4 Mo.	8 Mo.	4 Mo.	8 Mo.	12 Mo.	4 Mo.	8 Mo.	12 Mo
1415-29-A	Chloride	12632	87	Flat	10	6C	3C			
1415-29-C	Sulfate	"	84	Flat	10	3C	1C	73	20	
1389-70-A	Modified sulfate	"	68	Flat	5B	2CB	0			
W-487 (Harmon Gold Drops)		"	96	38	10	10	10			
Polymer K (P-253-R-076761)		"	78	Flat	10	5C	5C	66	24	
Argent Gray (P-253-U-015166)		"						41	30	
Complementary Blended Control		"						53	20	
AGI-734-D; 37226	Sulfate	"	Four Months exposures in masstone and metallic formulatio							
AGI-734-D; 1576	Sulfate	"	be available by 7/15/53 in exposure series TX-5147.							
BGI-734-D; 1578	Modified chloride	"								
BGI-734-D; 1579	Modified chloride	"								

* P/B ratio of chromium hydroxide = 15.4/100

Ratings: Exposed gloss - 60° readings; DuPont Universal Glossmeter.

Film Integrity - 10 = no failure; 0 = Severe failure.
B = blistering; C = Checking

Polish Back - 10 = polishes to original gloss
0 = no polish back gloss

TABLE III

EFFECT OF REPLACEMENT OF W-701 OR CLEAR BASE BY CHROMIUM HYDROXIDE ON FLORIDA DURABILITY IN "DUCO" METALLICS

Formula			286-55658 "Metallichrome"					272-57095 Glamor Metallic						Experimental Metallic			
Prime Pigments (plus aluminum)	Clear Base (% of enamel)	Exposure Series	Exposed Gloss			Film Integrity	Polish Back	Exposed Gloss		Film Integrity		Polish Back		Exposed Gloss		Polish Back	
			4 Mo.	8 Mo.	12 Mo.	12 Mo.	12 Mo.	4 Mo.	8 Mo.	8 Mo.	12 Mo	8 Mo.	12 Mo.	4 Mo.	8 Mo.	4 Mo.	8 Mo.
W-785/1415-29-C*	0%	12632	68	42	23	10	10	51	10	7B	3B	6	1				
W-701	0%	"	86	75	63	10	10	45	10	10	7B	8	4				
W-785/W-485	65%	"	66	38	18	10	10										
W-785	80%	"						20	10	3B	1B	3	0				
W-785/1415-29-A**	0%	12711												47	14	10	8
W-701	0%	"												54	28	10	10
W-785	50%	"												23	10	10	6

* 69% 1415-29-C (Sulfate process) used in 286-55658
81% 1415-C used in 272-57095

** 75% 1415-29-A (chloride process) used in experimental metallic. Percents are based on pigment.

Ratings: Exposed gloss - 60° readings; DuPont Universal Glossmeter

Film Integrity - 10 = no failure; 0 = severe failure
B = blistering; C = checking

Polish Back - 10 = polishes to original gloss
0 = no polish back gloss

TABLE IV

FLORIDA DURABILITY OF CHROMIUM HYDROXIDE IN "DULUX" MASSTONE

Pigment	Process	Exposure Series	P/B Ratio	192 Line-RC-3101/RC-718 (baking)				93 Line (air dry)			
				Exposed Gloss		Film Integrity		Exposed Gloss		Film Integrity	
				4 Mo.	8 Mo.	4 Mo.	8 Mo.	4 Mo.	8 Mo.	4 Mo.	8 Mo.
AGI-734-D Lot 37226 (Flushed)	Sulfate	12817	10/100	92	74	10	3B				
		"	15/100	89	80	10	5B				
		"	20/100	90	78	9B	2B	88	49	3B	1B
		"	25/100	90	74	7B	2B				
AGI-734-D Lot 37261 (Dry)	Sulfate	"	10/100	94	78	8B	2B				
		"	15/100	93	75	10	10				
		"	20/100	93	76	10	10	91	48	10	7B
		"	25/100	91	78	10	5B				
Polymer K	--	"	15/100	89	90	10	10				
W-701	--	"	192 line 26/100 93 line 20/100	86	90	10	8B	91	42	10	10
W-403	--	"	20/100	99+	88	10	10				

AGI-734-D;	1576	Sulfate	TX-5193	Four months exposures in masstone and in metallic formulations will be available by 8/15/53.
BGI-734-D;	1578	Modified chloride	TX-5193	
BGI-734-D;	1579	Modified chloride	TX-5193	

Ratings: Exposed gloss - 60° readings; DuPont Universal Glossmeter (read over 65-1052 primer)

Film Integrity - 10 = no failure; 0 = severe failure
B = blistering; C = checking

TABLE V

CHROMIUM HYDROXIDE ACCELERATED* BLISTER TESTS PLANT AND SEMI-WORKS PIGMENT SAMPLES

Pigment Code	Process	"DUCO" MASSTONES**				"DULUX"	
		Unexposed		1 Mo. Florida Exposure Series TX-5147		Unexposed	
		Initial Blistering	Blistering at 168 Hr.	Initial Blistering	Blistering at 168 Hr.	Initial Blistering	Blister at 168
AGI-734-D:"Duco"-Lot 37226: "Dulux"-Lot 37261	Sulfate	None	0	None	0	72 Hr.	1 AA
AGI-734-D, Lot 1576	Sulfate	None	0	None	0	None	2 AA
BGI-734-D, Lot 1578	Modified Chloride	None	0	None	0	None	2 A
BGI-734-D, Lot 1579	Modified Chloride	None	0	None	0	72 Hr.	1 AA
W-701 Control(B#5218462)	---	48 Hr.	1B	None	0		
W-701 Control(B#4513238)	---	None	0	48 Hr.	2D		
W-487 Control(B#4724132)	---	None	0	None	0		
W-701 Control	---					24 Hr.	2 C
W-487 Control	---					72 Hr.	5D

* Panels immersed in distilled water at 98°:
UNDERCOAT: "DUCO" - 475-1195 Primer; 683-1717 Surfacer
"DULUX" - 765-1676 Primer Surfacer

RATINGS: Numerical ratings refer to number of blisters: 0= None, 10= Dense
Letter ratings refer to size of blisters: AA= Very small, D= Large

** NOTE: "Duco" metallic formulations immersed after one month Florida exposure did not blister.

TABLE VI

EFFECT ON WORKING PROPERTIES OF "DUCO" METALLICS OF REPLACEMENT OF CLEAR BASE BY CHROMIUM HYDROXIDE

Code	Formulation	Hiding (sq ft/gal)	Scaling*	Mottling*	Patching*
F-281-X-89458	Control color 0785/0594/0913/094/B-614/B-613 10/20/3/17/5/45	619	5	5	5
F-281-X-89459	Control color + clear base	359	5	5	5
F-281-X-89460	Control color + chromium hydroxide	433	5	5	5
F-281-X-89461	B-613 in control color replaced by chromium hydroxide	479	5	5	5

Note: Chromium hydroxide sample AGI-734-D Lot 1576 was used in this working property evaluation.

*Rating: 1 = Excellent
5 = Very poor

TABLE VII

STABILITY OF CHROMIUM HYDROXIDE PLANT SCALE AND SEMI-WORKS PIGMENT SAMPLES

Pigment	Viscosity Stability*									Settling	
	"Dulux" Mill Base			"Dulux" Enamel			"Duco" Lacquer			"Dulux" Mill Base and Enamel (2 Mo. Shelf)	"Duco" Lacquer (2 Mo. Shelf)
	Initial	2 wk. 110°F	2 Mo. Shelf	Initial	2 wk. 110°F	2 Mo. Shelf	Initial	2 wk. 110°F	2 Mo. Shelf		
AGI-734-D; "Duco" lot 37226 "Dulux" lot 37261	420	370	430	155	150	100	1630	850	1340	Soft	None
AGI-734-D; 1576	400	320	400	170	110	180	1700	805	1350	Very Soft	None
BGI-734-D; 1578	1179	3700	1270**	164	122	195	1750	830	1530	Very Soft	None
BGI-734-D; 1579	1495	5000	1810**	167	128	192	1545	815	1415	Soft	None
W-701	57	57	57	108	104	108	1060	830	1005	Very hard	Soft

*Viscosities are in centipoises determined by the Brookfield Viscosimeter (average of readings at 10 and 20 r.p.m.)

**Livered on surface

Notebook Reference: "Duco" N.B. 666 page 128

"Dulux" N.B. 666 page 158