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

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

LEMON YELLOW - Y-524-D
DEVELOPMENT OF "B" PROCESS

Period Covered: SEPTEMBER 1947 - FEBRUARY 1950

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

TITLE: LEMON YELLOW - Y-524-D
DEVELOPMENT OF "B" PROCESS.

PERIOD COVERED: Sept. 1947 - Feb. 1950.

CHARGE: 11-3
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SUBMITTED BY: R. R. Denslow 2/10/50 DATE SUBMITTED: 2/10/50

APPROVED BY: B. H. Perkins 2/20/50 DATE ISSUED: 2/20/50

INTRODUCTION:

This report represents a summary of the work carried out intermittently during the period September 1947 to February 1950 on the development and standardization of the high strength lemon yellow, Y-524-D. The early work (1940-1941) is covered in KN-41-28.

A plant formula was prepared recently and much of the following material has been taken from the standard formula notes. Additional information will be found in the laboratory notebooks and "DSN" records (see references below).

PATENT SITUATION:

There appears to be nothing patentable in either this new process or the product.

SUMMARY:

In connection with a Sales Service problem, a brief laboratory study was carried out some years ago (circa. 1940) aimed at developing a yellow similar to Calco's Lemon Yellow 40-2540 for use in the preparation of greens. This resulted in a formula, K-1164, which was taken to the semi-works for further study. A number of batches were made embodying several variations and one (lot 4166) was set up as a standard (SD-48105). The semi-works process was coded as K-1274 (AY-524-D). As the result of a decision by the customer (Adelphi Paint) to use Chrome Green rather than yellow/blue and because of the pressure of more urgent items, work on this problem was discontinued early in 1941.

The 40-2540 yellow has continued to enjoy wide use (largely in ink) and in 1947 a decision was reached to set up a counter-offering by standardizing Y-524-D in the plant. The specific objective was to submit an offering to Intag (Lodi). Eleven batches were made (Oct. - Dec. 1947) with only fair success and the best mix which could be made (lot 84577) was rejected by Sales on the grounds of redness of tint.

The problem was given active attention in the laboratory and semi-works during the Spring of 1948 and a plant batch (57451) was made in May. This was a "flop" possibly because of an error in the PbO/HAc analysis. After further laboratory and semi-works study, another plant batch (62067) was made in November. It was satisfactory on control but the finished product showed bad darkening as a varnish drier rubout was allowed to dry. This poor "stability" was shown to be due chiefly, if not entirely, to moisture in the pigment. Redrying in the plant (lot 89043) was unsuccessful; however, a barrel redried in the semi-works (lot 89296) was fairly satisfactory and while inferior to the old semi-works standard or semi-works production was accepted by Intag and has been used recently as a temporary standard. Six additional 5-mole plant batches were made in the latter part of 1949 under close supervision by the Chemical Division; no unusual difficulties were encountered. They were checks to lot 62067 (89296) and showed fairly good reproducibility. The formula used is the basis for the present "B" process.

DISCUSSION:

General

Y-524-D is a "lemon" yellow greener in masstone and reflected undertone than Y-318 (554)-D but redder than Y-202-D. For its masstone, it is relatively green in tint and strong. Like other typical lemon yellows the masstone is dark (small particle size?) and a tendency is observed in some samples for the masstone to become even darker as the exhibit ages. Its light stability is poor. The chief use of the pigment is in printing ink, although, as mentioned above, it has been given consideration as a shading yellow for paint.

The proposed standard, now being evaluated by Sales Service, is lot 506 and is made up as follows. (Reference: letter Denslow - Spengeman, 1/17/50).

Y-524-D, NS-494 (part of 72088)	200 lbs.
Y-524-D, NS-495 (part of 72071)	200 "
Y-493-D, 13490 (SSS)	5 " (see note)
	405 "

(Note: The Y-493-D was added to more closely approach the temporary standard, lot 89296).

Y-524-D is similar to Calco's 40-2540 and our Y-599-D. Readings (Varnish Drier rubouts) of lot 506 made in the Sales Service Laboratory are presented below.

	Y-524-D, lot 506 vs			
	Y-524-D, SD-48105 (1)	Y-524-D, 89296 (2)	Y-599-D, 67985 (3)	40-2540 C-51400
Masstone (wet)	green, vs dull	lt., int.	vvs green	vvs/vs green
" (dry)	dark, dull	s.lt., s.red	s.dark	vs dk, vs grn.
Undertone	O.K.	O.K.	O.K.	O.K.
Strength (4)	105	O.K.	98	102
Tint	vs.red	vvs green	vs grn., vs int.	vvs red

(1) Original semi-works standard. See KN-41-28.
(2) Temporary standard for Intag.
(3) Proposed standard.
(4) The strength differences shown in the last three columns are of questionable significance.

Like Y-202-D and Y-599-D, Y-524-D uses basic lead acetate liquor as a raw material. The choice is based on economic considerations; litharge can be used and possibly lead nitrate, but indications have been that either of these would give a higher ingredient cost.

As indicated above, difficulties were encountered in initial attempts to operate the "A" formula (Ref. KN-41-28) on a plant scale and it was impossible to match the semi-works standard satisfactorily. This was due to a number of causes some of which are discussed below. The basic trouble, however, was probably the result of too large a batch size together with the high chromate/lead ratio and the very close "acid balance" used to get high tinting strength. Difficulties were also encountered in the laboratory, attributable to the same causes and further complicated by uncertainties in the analytical composition of the lead acetate liquor used in some of the experiments. Semi-works operations were reasonably satisfactory and served as the best means for evaluating the effect of process variables.

The pigment is made striking a bichromate/chromate mixture (plus a small amount of sodium purophosphate) into basic acetate liquor (TBL) adjusted with acetic acid to a definite acidity. The strike is made under the surface as rapidly as possible (consistent with adequate mixing) precipitating about 89% of the lead as chromate and pyrophosphate. The excess lead is precipitated (as lead sulfate) by alum which is followed in turn by additional phrophosphate and soda ash forming, respectively, aluminum phosphate (pyrophosphate?) and "alumina hydrate". A stoichiometric analysis of the formula is given in Appendix I.

The process as finally standardized (Y-524-D(B)) differs from the previous standard ("A") formula, K-1274 set up in 1941 on the basis of semi-works operation in the following respects:

1. The batch size has been cut from 6 to 5 moles.
2. The Chrome/lead ratio has been cut about 5%.
3. The quantity of (total) acetic acid has been increased.
4. Drying conditions have been changed.

The comments below are quoted from the standard formula notes on the "B" process:

"Making Operations

While the present formula is apparently more stable than the "A" process, it is sensitive to relatively slight variations in the ratio of ingredients and proper care should be observed in checking weights and using the correct analyses of solutions. Too little acid or absence of a lead excess after striking, for example, may result in a "flop", viz. very red pigment of poor lightfastness which is difficult to consume in other codes.

"One of the more likely sources of difficulty is in the PbO/HAc analysis. For this reason, a new analysis is made of the lead liquor after pumping up the first portion to the scale tank. The weight of the second portion of lead and of the supplementary acetic acid is based on the new analysis if it varies appreciably from the original analysis or on an average of the two. Both portions of lead liquor should come from the same make.

"The pH of the diluted lead solution (ready to strike) is about 6.8-7.0. It cannot be used as an exact control point since it does not change much with changes in acetic acid. It should serve to detect gross errors; for example, a pH much above 7.0 would indicate a deficiency in acid which might be serious.

"To obtain the proper strike pH it is necessary to have not only the PbO/HAc correct but the chrome/bichrome solution should be adjusted carefully to the designated pH (6.0-6.1). With the N-8/N-10 ratio at 600#/50#, about 5-10# of N-7 is required. Future experience may make it possible to reach the same endpoint by changing the N-8/N-10 ratio and omitting the N-7.

"The green vats (260-261) are used for the strike because of their good agitation and facilities for under-surface addition of the chrome/bichrome. Recent manufacture has been at the 5-mole batch size. It is not known whether a higher concentration can be used and any attempt to increase batch size should be made cautiously.

"Semi-works experience indicated the desirability of a rapid strike. Scale tank 361 (used for the chrome/bichrome solution) requires about 13 minutes to empty with the valve wide open. During the first 6-7 minutes the pH remains fairly constant at about 7 (it may rise to ca. 7.1) after which it starts to drop and at 9-10 minutes, it drops rapidly to about 6. During the last few minutes it drops more slowly to a final figure of 5.7-5.9. Experimental (semi-works) batches have been made with as little as 350 lbs. HAc per 1115 lbs. PbO. With this amount of acid, the pH dropped to about 6.2 and rose slightly at the end to 6.4. While it gave material of satisfactory quality, it was probably in the danger zone and with a little less acetic acid the lead excess would disappear, the pH would rise to 7 or higher and the batch would flop. The formula directs that a quick test be made for xs lead and if negative an extra (emergency) portion of acetic acid is added. This emergency treatment should help to eliminate "flops" due to some unsuspected error in the PbO/HAc/CrO_4 ratio. Until more manufacturing experience has been accumulated it is recommended that, in addition, a second operator determine the pH of the slurry at the end of the strike and if it is higher than 6.3, add the extra acetic acid even though the lead xs is O.K. A lead excess is, of course, essential.

"As in the preparation of other "lemon" yellows, delays in the addition of solutions should be avoided and the batch should be sent to press promptly when finished. The alum, pyrophosphate and soda ash solutions should be prepared and ready before starting the strike and added without delay as indicated in the formula. The making supervisor should check with the press room before striking to make certain that the press is ready to receive the batch.

"Only limited information is available on the effect of final pH. If too low (e.g. 5.6), the pigment filters very slowly; if too high (6.5 or higher) there is apparently a tendency towards redness.

"Pressing and Drying Operations
As indicated above, processing of this pigment should be carried through promptly. The press should be set up before starting the batch and pressing started at once. Because of small particle size, pressing is occasionally rather slow with some tendency to bleed.

"The color is only washed for two hours. However, at the present batch size, this appears fairly effective. "Water soluble salts" in the standard lot were reported as 0.56%. Ohm readings on the filtrate have not given consistent results.

Lot 62067 - 3000 ohms.
70670 - 9000 ohms (4 hrs.)
70695 - No reading reported
72034 - 350 ohms
72071 - 400 ohms
72088 - 500 ohms

"Complete drying of the pigment is essential. Under-dried material gives an ink which darkens badly as the exhibit ages. High moisture might also be expected to give abnormal "working properties" in certain vehicles. 24-30 hours at 190°F in the HV dryer is specified. However, the color should be checked before pulling to make certain it is actually dry. The only known effect of over-drying is a slight tendency towards a darker, redder masstone. If difficulties are encountered with a simple "feel" test, consideration should be given to setting up a "Brabender" test.

"As in the case of other light yellows, care should be taken to avoid contamination.

"Grinding Operation.
No difficulties have been encountered in part of the process in the course of the development work.

"The remarks (above) on drying should be borne in mind and care should be observed that lump color is not damp. Attempts to re-dry pulverized color have not been satisfactory.

"Care should be observed to avoid contamination."

REFERENCES:

Additional information can be found in Notebooks 1053, 1281-X and 1305 and in the DSN records. The semi-works studies leading to the "A" formula are reported in KN-41-28.

APPENDIX I

INGREDIENT BALANCE, COMPOSITION AND YIELD:

The "strike acidity" and "precipitant balance" of ingredients reacting with the lead are tabulated below. The assumed chemical composition (qualitative and quantitative) obtained from one mole of PbO is also shown. (Ref. 1305-42).

Weight	Ingredient	Strike Acidity	Lead Precipitants	Moles Product per mole PbO
223	PbO (1 mole)			
76	Total HAc	1.265		
120	Bichromate (1)	0.805	0.805	0.805 $PbCrO_4$
10	Chromate (1)		0.0672	0.0672 "
2.4	Sod. Pyrophosphate		0.0180	0.00902 $Pb_2P_2O_7$
32	Alum (100%)		0.144	0.112 $PbSO_4$
3	Sod. Pyrophosphate			0.00375 $Al_4(P_2O_7)_3$
ca. 16	Soda Ash			0.0406 "Hydrate" (2)
Total equivalents/mole PbO		2.070	1.034	
			0.890 (in strike)	

(1) As $Na_2Cr_2O_7.2H_2O$

(2) Mol. weight 207, i.e. "hydrate" yield assumed to be 1/3 the weight of "as is" (107%) alum used.

The calculated composition and goal yield from the above are as follows:

	Pounds/batch	Percent
$PbCrO_4$	1410	83.8 calculated
$PbSO_4$	169	10.1 "
$Pb_2P_2O_7$	26.5	1.6 "
$Al_4(P_2O_7)_3$	11.8	0.6 "
Hydrate (m.w.207)	42.	2.5 "
	1659.3	

(Continued on page 7)

	Pounds/batch	Percent
Total forwarded	1659.3	98.6
Water soluble salts	9.4	0.56 (by analysis)
Moisture	13.4	0.80 " "
Calc. Goal Yield	1682.	99.96

The percent of $PbCrO_4$ in the standard mix (lot 506) by chemical analysis is 84.77%. This corresponds to an (analytical) goal yield of 1665. This is believed to be more reliable than the calculated figure; the anhydrous goal yield has therefore been set at 1652 pounds.

The available figures on actual yields (from the plant records) are as follows:

Lot	Yield
62067	1642
70670	1525
70695	1591
72034	1619
72071	1622
72088	1634

APPENDIX II

Standard making formula and processing data attached.

CODE: Y-524-D (B) K#

GOAL: 1665# SIZE: 5 MOL.

DIAZO VAT:

COUPLING VAT:

STRIKE VAT: 260, 261

STD. HOURS 3.9 NON-BLEEDING.

APPROVED BY:
JB: 2-7-50
HA: 2-7-50
CWO: 2-7-50
GL: 2-7-50
JPL: 2-16-50

VAT	NAME: INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS
	NOTE: EVERY ATTEMPT SHOULD BE MADE TO WEIGH BOTH LEAD LIQUOR PORTION FROM THE SAME "MAKE". BATCH MUST PRESS IMMEDIATELY-CHECK PRESS ROOM BEFORE STRIKING.			
350 1	1. RUN INTO SCALE TANK 350			
	M T R %	7500	64	0
	%		262	0
	2. TAKE SAMPLE AND DELIVER TO LABORATORY FOR CHECK ANALYSIS.			
S.V. 2	3. RUN 15" (1320G.) WATER INTO STRIKE VAT.			
	4. RUN SCALE TANK 350 INTO STRIKE VAT.			
Misc 3	5. WEIGH AND HOLD AT SCALE TANK 361 FOR STEP 35	12	479	12
	6. WEIGH AND HOLD AT STRIKE VAT FOR STEP 25	15	479	12
	7. WEIGH AND HOLD AT VAT 365 FOR STEP 20	150	15	150
	8. WEIGH AND HOLD AT VAT 362 FOR STEP 31	80	3	80
	9. WEIGH AND HOLD AT STRIKE VAT FOR EMERGENCY USE IN STEP 44 (15# 100%) %		30	
350 4	10. RECORD: STEP 2 ANALYSIS R % N-64			
	% N-262			
	11. AVERAGE STEPS 1 AND 10 AND USE TO CALCULATE AMOUNT WEIGHED IN STEP 1 %	0	64	± 900
	%		262	± 162
	12. RUN INTO SCALE TANK 350 ADDITIONAL LEAD LIQUOR TO TOTAL 1115# FOR STEPS 11 AND 12			
	M T R %		64	± 215
	%		262	± 38
S.V. 5	13. RUN SCALE TANK 350 INTO STRIKE VAT.			
	14. ADJUST TOTAL ACETIC ACID TO 380# M %		30	± 180
	15. WHEN USING VAT 261, SET AGITATOR AT 21 R.P.M.			
	16. ADJUST TO 58" (5104G.) AT 68-72°F.			
	17. TEST AND RECORD: pH , NORMAL 6.8-7.0.			
365 6	18. RUN 17" (75G.) WATER INTO VAT 365.			
	19. TURN ON AGITATOR AND STEAM.			
	20. DUMP IN N-15 WEIGHED IN STEP 7.			
	21. HEAT TO 80-120°F.			
	22. STIR 5 MINUTES OR LONGER TO DISSOLVE.			
DRUM 7	23. RUN ± 30 G. WATER INTO DRUM.			
	24. TURN ON STEAM.			
	25. DUMP IN N-479 WEIGHED IN STEP 6.			
	26. HEAT TO 80°-110°F.			
	27. STIR 5 MINUTES OR LONGER TO DISSOLVE.			
	28. HOLD AT STRIKE VAT CHUTE FOR STEP 47.			
362 8	29. RUN 6" (72G.) WATER INTO VAT 362.			
	30. TURN ON AGITATOR AND STEAM.			

CONTINUED ON PAGE 2.

VAT	PAGE: 2 CODE: Y-524-D(B) LBS: 1665# INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS.
	31. DUMP IN N-3 WEIGHED IN STEP 8.			
	32. HEAT TO 80-120°F.			
	33. STIR 5 MINUTES OR LONGER TO DISSOLVE.			
361	34. RUN 15" (250G.) WATER INTO SCALE TANK 361.			
9	35. DUMP IN N-479 WEIGHED IN STEP 5.			
	36. STIR 5 MINUTES OR LONGER TO DISSOLVE.			
	37. RUN IN M T %		8	600
	38. RUN IN M T %		10	50
	39. ADJUST TO 57"(950G.) AT 68-72°F.			
	40. TEST AND RECORD: pH , NORMAL 5.8-6.0.			
	41. IF NECESSARY, ADJUST TO pH 6.0-6.1 WITH N-7 OR N-33		7	± 8
	RECORD: pH .			
S.V.	42. STRIKE SCALE TANK 361 AT 68-72°F. INTO STRIKE VAT			
10	AT 68-72°F UNDER THE SURFACE, THROUGH THE DISTRIBUTOR			
	IN 12-14 MINUTES.			
	43. WASH IN SCALE TANK 361 IN + 2 MINUTES.			
	44. WHILE WASH WATER IS RUNNING IN, TEST AND RECORD: SPOT			
	PAPER TEST FOR PbXS , MUST BE S.+TO +. USE			
	4% SODIUM SULFIDE SOLUTION. IF NEGATIVE DUMP IN N-30			
	WEIGHED IN STEP 9.			
	45. IMMEDIATELY AFTER COMPLETING STEP 44, RUN VAT 365 INTO			
	STRIKE VAT IN 2 MINUTES.			
	46. STIR 1 MINUTE WHILE WASHING IN VAT 365.			
	47. POUR IN DRUM OF N-479 IN 1-2 MINUTES.			
	48. STIR 1 MINUTE WHILE WASHING IN DRUM.			
	49. RUN IN VAT 362.			
	50. STIR 5 MINUTES.			
	51. TEST AND RECORD: pH , NORMAL 5.9-6-3.			
	52. IF NECESSARY, ADJUST TO pH 6.1-6.4 WITH N-3 OR N-33.			
	RECORD: pH .			
	53. FLOOD TO 85" (7400G.).			
	54. PRESS AT ONCE WITHOUT AGITATION.			
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