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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

Scarlet Lake RE-542-D
Laboratory Variable Study.

Period Covered: November 11, 1943 to May 3, 1944.

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: Scarlet Lake RE-542-D
Laboratory Variable Study.

Period Covered: November 11, 1943 to May 3, 1944.

SUBMITTED BY: J. B. Callaway J B Callaway DATE SUBMITTED: 5-9-44

APPROVED BY: Alfred Siegel Alfred Siegel 6/21/44 DATE ISSUED: 6-23-44

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INTRODUCTION:

In earlier exploratory work, reported in KN-42-166, it was discovered that the mixed barium-aluminum pigment of the dye, 6-chlor-2-amino-toluene→R-salt, laked on alumina hydrate and barytes, gave an approximate match to Scarlet Lake RE-85-D. This product, K-1729, was found to be superior to RE-85-D in lightfastness. A few charges of K-1729 were made in the semi-works and samples submitted for evaluation to Newburgh, F&F Department, under the code, RE-542-D. Newburgh approved the lake as an acceptable substitute for the Scarlet 2R type lake RE-85-D.

It was decided to return the formula to the laboratory for detailed study of the variables before carrying out extensive development. This report covers the laboratory work carried out on the formula.

SUMMARY AND CONCLUSIONS:

1. The laboratory variable study on K-1729 has been completed and a "direct laking" procedure, K-2016, has been developed. K-2016 differs in several minor details from K-1729 (see formula and formula notes appended) but principally in eliminating isolation of the dyestuff.

2. Tinctorial comparisons:

	Masstone	Undertone	Tint	L/F
K-2016 versus RE-542-D (K-1729).	vs dark	s.strong	s.strong vs int.	approx equal
K-2016 " RE-85-D	light, vs yellow	sl.strong	strong	superior M.T. & Tint

3. The principal variable for control of undertone and tint hue is the pH for strike. The optimum pH for the dye slurry prior to strike appears to be between 2 and 3. It has been found most feasible to maintain this level by allowing the dye coupling to finish at a pH in the neighborhood of 2-3 and adjusting to the desired pH with acetic acid or caustic soda as required. In general, a pH below the optimum level produces slightly lighter yellower masstones, yellower and slightly weaker tints. Above the optimum level, slightly darker and bluer masstones, bluer and stronger tints are obtained. The darker, bluer material is superior in lightfastness to the lighter yellower type.

4. Discussion of other process variables will be found in notes attached to the "K" formula at the end of this report.

5. K-2016 was set up using National Aniline R-Salt. A change over to Calco intermediate, now available on the plant, gave light masstone and yellow tint material on the formula. The

application of the pH variable eventually produced an approximate match for the "K" sample but the lakes are on the defensive in being somewhat duller and bluer in undertone and tint.

GENERAL DISCUSSION:

The filtration of the dye slurry as specified in K-1729 procedure was difficult and objectionable owing to the slimy gelatinous nature of the dye. It has been found satisfactory to eliminate the filtration provided pH of the dye slurry is adjusted before laking, as specified in K-2016.

The amine has been found to dissolve in the hydrochloric acid solution at room temperature with agitation. However, upon continued agitation the amine-hydrochloride separates from solution but upon addition of sodium nitrite the soluble diazonium salt is formed and a clear solution results. The sulfamic acid used in K-1729 has been eliminated as probably unnecessary for improvement of tinctorial properties.

Reduction of the R-Salt excess from 10% to 5% apparently has no effect tinctorially. The use of caustic soda rather than soda ash in dissolving the R-Salt was desirable because the former resulted in more easily controlled pH.

The substitution of re-slurried #3 LC Alumina Hydrate for freshly prepared base was unsuccessful in several experiments. A bluer tint pigment was invariably formed which could not be shifted toward the yellow shade necessary to match RE-85-D by application of process variables. Although it was found necessary to wash the freshly precipitated hydrate base required in the formula, aging of this base for as much as 14 days apparently had no detrimental effect.

Employment of the mixed barium-aluminum precipitant used in K-1729 was found unnecessary in K-2016 since the same effect could be obtained by control of pH. However, in one experiment in which Calco R-Salt was used, a mixture of 18 grams of barium chloride and 0.5 grams of alum for an 0.025 mol strike was effective in obtaining a desired shift to a yellower hue.

EXPERIMENTAL DETAILS:

Notebook 1076 Expts. 1 to 41;
Notebook 1097 Expts. 1 to 9.

1. Volume variations 1076-21, 26, 27.
2. Temperature variations 1076-19, 23, 24; 1097-4
3. Alumina Hydrate bases 1076-18, 19, 20, 24, 26.
4. Variations of pH for coupling 1076-19, 20, 21, 36; 1097-7.
5. Variations of pH for strike 1076-31, 32, 34, 35, 38; 1097-1, 2, 3, 4, 6, 7, 8.
6. Coupling variables. 1076-29, 25, 33, 36, 40; 1097-1 9

K-13398

FORMULA SHEET

DUPONT

COLOR CODE DATE 5-3-44 NAME Scarlet Lake K- 2016 (Rept)

OBJECT "Direct Laking" procedure for NE-542-D)

BASED ON Laboratory procedure 1077-9

BATCH SIZE-MOLS. 0.25 BATCH No. OF "K" SAMPLE 1076-370

LBS. OR GMS.	MATERIAL	100%-WT.	GAL.	C. C.	MANIPULATION	N/
27.5	Muriatic Acid 100% (±31.5% HCl solution)	27.5	90	750	Dilute to at 75°F. Add with agitation	28
35.5	2-amino-6-chlor-toluene "as is" (OH-8160) .99 1/2% by Nitrite value.					527
					Stir 15 minutes. To 32°-35°F. with	
±800	Ice				Add rapidly (±3 minutes)	57
17.5	Sodium Nitrite "as is" (99.7% $NaNO_2$)	17.5	12	100	dissolved in and cooled to 32°F with	5
25	Ice				Stir diazo 15 minutes or until clear solution obtained, holding temperature at 35° ±3°F.	57
					Test: Positive on starch KI paper; positive on Congo Red paper.	
					Couple diazo in 30 minutes under surface into:	
					Add	
14	Caustic Soda 100% (±50% NaOH solution)	14	60	500	make to at 75°F. Add	7
114	R-Salt di soda salt (National Aniline OH-2696, 80.3% H_2O & 2 % Salts dried in laboratory at 140°F. and ultrapulverized)	91.4	120	1500	Make to at 75°F. and stir to solution in 30-35 minutes. Couple at 75°F. Stir dye slurry 30 minutes. Test: Negative test for excess diazo with β-naphthol solution; positive test for R-salt with diazotized tetrazo. Record pH (Normal 2.5 ±0.2) Make volume to	125
			1440	12000	at 75°F. Add	
10	Acetic acid 100% (±8% CH_3COOH solution)	10			Stir 5 minutes. Add the following separately prepared base:	30
383	Alum "as is" ($Al_2(SO_4)_3 \cdot 18H_2O$)	410	180	1500	Dissolve in at boil. Dilute with cold water to	15
			900	7500	Agitate and strike in 20 minutes with	
178	Soda Ash "as is"	178			dissolved in	3
			180	1500	at boil. Agitate 10 minutes.	
					Flood to	
			2880	24000	Draw 6 vatsful allowing hydrate to settle each time and reflooding to	
			2880	24000	Test: Negative test for SO_4 with $BaCl_2$ solution. Record pH (Normal 5.7 ±0.1)	

PACKAGE LBS. PER COST GROUP TYPE COLOR SIGNATURE

GOAL YIELD

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FORMULA SHEET
Page 2.

DUPONT

COLOR CODE | DATE 5-3-44 | NAME Scarlet Lake | K- 2016 (Expt)

OBJECT

BASED ON

BATCH SIZE-MOLS. | BATCH No. OF "K" SAMPLE

LBS. OR GMS.	MATERIAL	100% WT.	GAL.	C. C.	MANIPULATION	N/
					Agitate 5 minutes. Add	
685	Baryten "as is"				slurried in	17
			72	600	water at 70°-75°F and screened (40 mesh). Total volume	
			2388	19000	at 77°F. Strike in surface in 10 minutes with	
180	Barium Chloride "as is"				dissolved in	16
			180	1500	at 70°-75°F. Agitate at 77° ±2°F. for 15 minutes. Tests Record pH (Normal 4.5 ±0.2) Heat to 161°F. in 15-20 minutes. Hold at 161°F. for 5 minutes. Record pH (Normal 4.8 ±0.2). Cascade to 140°F. Press. Wash chloride free. Dry at 140°F. Pulverize as for BE-85-D.	

Calculated Composition
(on basis anhydrous yield)

Barium salt of dye	=	16%
Alumina Hydrate base	=	10
Barytes	=	74
		100%

PACKAGE 250 LBS. PER polyweave drum | COST GROUP 6 | TYPE COLOR BE-85-D | SIGNATURE J.P.Callaway

GOAL YIELD 95% "as is" | 92% anhydrous (Ref. 1076-31)

Notes to K-2016 (Expt)

1. This formula is a revision of RE-542-D (K-1729) and differs from the latter principally in the following respects:

(a) excess R-Salt is reduced from 10% to 5%.
(b) caustic soda replaces soda ash in the coupling.
(c) the amine is dissolved in hydrochloric acid solution at room temperature.
(d) the coupling is finished in acid medium.
(e) filtration of the dye is eliminated.
(f) the alumina hydrate base is changed from a 30/15 to a 30/13 type.
(g) the mixed barium chloride/aluminum sulfate precipitant is replaced by all barium chloride.

2. The following variables have been found to be the most effective in control of tint and undertone hue:

pH for strike

It has been found that a dye slurry of pH 2.5 ±0.2 will produce the hue of tint and undertone required to approximate those of RE-85-D. Using the National Aniline R-Salt as specified in the formula, the pH before strike ran between 2.5 to 2.9. Using Calco R-Salt, however, it has been found necessary to omit acetic acid and adjust pH of the dye prior to strike with ±5 lbs. of caustic soda per 0.25 mol strike; pH after strike is 5-5.5. Lakes obtained by this adjustment have been duller and slightly weaker than those obtained using the National Aniline R-Salt on the formula as written.

Temperature for Strike

Increasing temperature of strike from 77° to 105°F gave increasingly darker masstones, stronger and bluer tints. Above 105°F., however, very dark, dull masstones and dull tints resulted. The temperature control variable appears to be safe to use within the limit of 77°-100°F.

Increase in temperature for development from the formula level of 167°F, to the boil had little effect tinctorially.

Alumina Hydrate Base

Change of type base to a 30/15 gave bluer products which were too far out of line to approximate RE-85-D. The use of reslurried #3 LC Hydrate invariably gave much bluer products than the freshly precipitated 30/13 type base used in the formula. Considerable weakness was obtained in the lakes in which poorly washed hydrate base was used. In the laboratory it appeared to be necessary to drain the six waters from the base before use in order to obtain optimum results.

pH for Coupling

It is possible to carry out an "all alkaline" coupling ending at pH ±8.5. Reduction of the pH level to 2.3, as is required for the strike, may be done by the use of acetic acid. However, it was found difficult in the laboratory to adjust this pH accurately and the tinctorial results were in some cases inferior to those obtained using the dye made at a lower pH.

Quality of R-Salt

Most of the laboratory work was done with National Aniline R-Salt. For laboratory purposes, the R-Salt was dried at 140°F. and analysed for G, R and S-Salts (KCR-88). Although the Calco R-Salt used (CU-3771) differed by only ±2% from the previous National Aniline material, and not significantly in quantity of free acid present, the resulting lakes on the formula, as written, were too yellow for consideration. As indicated above, elimination of acetic acid and adjustment with caustic soda brought the Calco R-Salt lakes in line with those produced from National Aniline material.

3. The following variables were found to have an indeterminate effect on the tinctorial properties of the lake:

Volumes of the dye slurry prior to strike.
a ±25% variation had little effect.

Volume for precipitant.
a ±50% variation had little effect.

Volume of Diazo and of R-Salt.
±50% variations had little effect.

Accessory Agents

The substitution of 5 mol per cent of G acid, Mono acid L or Mono acid F for the R-Salt produced bluer and stronger tints. However, these same effects can be obtained by simple formula variations.

Variation of Strike

No improvements were obtained by varying the time for strike. Reverse strike had minor effects on tinctorial properties.

4. Yield

The goal yield of 953 lbs. "as is" is based on the average of five 0.025 mol strikes run in a consistency series on the formula. Toluene distillation, KCR-123, gave an average of 2.8% moisture in the "K" sample. Brabender moisture determinations were somewhat higher, giving a 3.2% average. The average from toluene distillation was used in calculating the anhydrous yield. Reference should be made to 1076-37.

5. Alcohol bleed of the "K" sample is somewhat more intense than for RE-542-D (K-1729) but both are greater than RE-85-D.

6. Evaluations were carried out by rubout 1:1 in varnish drier, extensions 1:30 in zinc oxide.

	Masstone	Undertone	Tint
K-2016 vs RE-542-D	vs dark	strong	strong, vs intense
K-2016 vs RE-85-D	light	s.strong	strong, vs intense

The rubouts are sensitive to higher temperatures, turning dark and brown in masstone, dull in tint upon heating at 140°F. Upon cooling the material apparently returns slowly to its original color.

7. Sulfamic acid has been omitted from the diazotization procedure. It was found in the laboratory that excess nitrous acid had little effect on color.

8. Approximately 300 grams of laboratory material, 1076-37G have been sent to "K" files as "Original Sample".

VC 6-12-46