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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

JACKSON LABORATORY PIGMENTS GROUP REPORT

Lithosol Fast Yellow 3GD (YT562D)
(Ni Complex of p-Chloro-Aniline -> 2,4-Dihydroxy-Quinoline)
Formula Modifications K-2409, K-2410, K-2411

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JACKSON LABORATORY

Pigments Group Research Report

Lithosol Fast Yellow 3GD - YT562D
(Ni Complex of p-Chloro-Aniline -> 2,4-Dihydroxy-Quinoline)
Formula Modifications - K-2409, K-2410, K-2411

Submitted By - A. D. Reidinger Date Submitted - 12-24-46

Approved By - D. B. Killian Date Issued - 1-31-47

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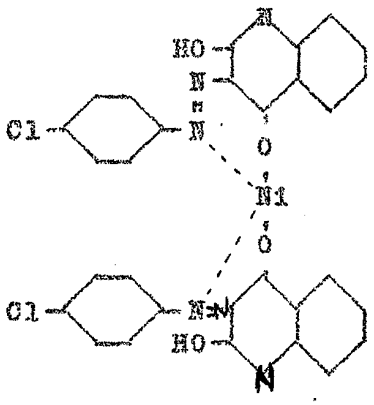
DUP050150694

Introduction:

Lithosol Fast Yellow 3GD, our YT562D, is a new pigment of greenish yellow shade developed at Jackson Laboratory, which represents an outstanding improvement in lightfastness compared to azo pigments in common use. It is prepared by coupling p-chloroaniline to 2,4-dihydroxy-quinoline in carbonate alkalinity, isolating the dye and converting it to the nickel complex. The product may be represented by the structural formula -



Molecular Weight
656

The present report covers the work done by the Pigments Group at Jackson Laboratory in studying the process.

Summary:

One objective of the work on this product was simplification of the formula in respect to operating details. This was accomplished by eliminating clarification of the coupling components and by omitting the isolation of the coupled dye, proceeding directly to the metallization stage from the coupling. Other changes made were reduction in the amount of sodium carbonate in the coupling, addition of all the caustic soda in one portion and reduction of time of metallization from three to two hours.

A formula K-2409 embodying these modifications has been written and a sample made up for evaluation by the Newark Laboratory. A copy of the K-2409 formula is appended to this report.

The product obtained differs from the original standard for YT562D in its greater depth of masstone but it is believed that this difference would not be important for most uses. Strength and tint are slightly superior.

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A sample of a "Ramapo" type of Lithosol Fast Yellow 3GD containing about 30% barium rosinate was also prepared. This product, K-2410, has no advantage in tinting strength even when compared on an equal tones basis, but is somewhat lighter in masstone and better in finish of ink drawdown.

For purposes of comparison, the nickel complex of p-nitroaniline -> 2,4-dihydroxy-quinoline was also made using the straight-through process described above. This sample, K-2411, is considerably darker and more olive in masstone than the chloro-counterpart, K-2409, but may be of interest because of its tinting strength. However, its redder tint may make it less desirable than YT562D as a toning color to produce green shades.

Discussion of Results:

Omission of clarification of the coupling components, as in K-2409, undoubtedly will depend on the quality of these intermediates. The p-chloro-aniline obtained from Monsanto Chemical Company contains a small amount of carbonaceous matter which effects the depth of masstone to a slight degree.

The dihydroxy-quinoline which is available for use at the Chambers Works contains considerable amount of impurities - foreign insoluble material partly carbon, and impurities formed in the manufacture of the intermediate. Clarification and recrystallization are required to obtain the quality needed to equal the present standard color. Unpurified DHQ produced darker, more olive masstones and redder tints, particularly when used in the straight-through process.

The reduction in the amount of sodium carbonate in the coupling was made to lessen the degree of foaming which occurs when the nickel chloride is added to the coupled slurry and to obtain a pH at this point approaching that found when isolated dye is used. Further reduction in amount of alkali tends to slow the rate of coupling. A pH of 7.6-9.0 at the end of coupling is considered a safe range. At pH 7.1, a darker, slightly weaker product was obtained.

Addition of all the sodium hydroxide required for metallization in one portion following the nickel chloride instead of at one half hour intervals appears to have no objectionable effects. The formation of the nickel complex occurs very readily in this instance and judging from the rapid change in color, neutralization of the acid formed can apparently be made with little delay. No difference was

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found when the stirring time at this point (before adding alkali) was varied from 2 or 3 minutes to one hour.

The pH range (6.5-7.0) specified in the formula is the same as in the original Jackson Laboratory process. It is recommended that the last part of the caustic soda be added carefully, testing with Blue Litmus paper until a very slight or negative test is shown. Excess alkali, for example pH 7.6 and 9.0, produces darker masstones and slightly weaker tints while at pH 5 yields were reduced by about 6%.

A 50% reduction in the amount of sodium acetate used resulted in a slightly darker masstone. However, since the product appeared to be more olive during the processing, no change was made from the formula amount.

Shortening of development period from three to two hours had no effect on tinctorial properties. Shorter periods, for example one half hour, gave a slightly lighter masstone which may be indicative of incomplete metallization and was consequently not considered advisable.

The "goal" yield of K-2409, based on two runs using analyzed intermediates was close to the theoretical.

Goal Yield "as is"	655 pounds (0.4% H_2O)
Goal Yield anhydrous	652 pounds
Theoretical yield	656 pounds

The "Ramapo" type lake, K-2410 and the PMA complex, K-2411 were made on a straight-through formula based on K-2409. No variable study was made except that it was found that the method of incorporating the rosinate in the lake, whether by precipitation onto the color or separate preparation and addition in slurry form, was not important.

Drying and grinding - Although no study was made of processing, the color does not appear to be effected by normal treatment such as drying at 80°C. and grinding in a mikropulverizer. The samples referred to in this report were pulverized at high speed and are probably finer and bulkier than is desirable. This is especially so in the case of the rosinate lake which shows bad dusting tendencies.

The Chambers Works Semi-Works process recommends that the pigment should be kept from overheating during grinding since it is

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ignited by sparks at 200-250°C. and burns readily when ignited. Special care should probably be taken in pulverizing the rosinate lake and the use of carbon dioxide may be necessary.

The meta- and ortho-isomers of p-nitro-aniline did not give pigments of any interest, the former being quite weak and the latter apparently not forming a metal complex under the usual conditions.

Other metals than nickel have also been tried, but none gave the intense green tint of the latter - the most promising being the copper complex which was an olive shade product with a red tint. The cobalt compound was a very dark olive pigment with dull red tint. The products obtained with chromium, titanium, zirconium and molybdenum were inferior in lightfastness and there is some question if metallic complexes were actually formed. Manganese, iron and zinc had previously been found at Jackson Laboratory to give products of poor lightfastness.

Experimental Details:

Details of individual experiments will be found in N.B. 1235. Additional information may be had by reference to Jackson Laboratory reports on Lithosol Fast Yellow 3GD (JLR-43-420, Nos. 1 and 2 and JLR-43-435, No. 1.

Ingredients Used

p-Chloro-Aniline is an extremely toxic intermediate, being more hazardous than most amino compounds in causing cyanosis, and all precautions should be taken to avoid contact with the skin or inhalation of its dust. It is supplied by Monsanto Chemical Company in drums in solidified form and must be broken into lumps for removal. It is recommended that this should be done out of doors or in a room where other people are not working. Spilled material should be cleaned up promptly.

p-Chloro-aniline melts readily when immersed in hot water (75-80°C.) and could be handled in a molten condition. Special equipment may be required to eliminate the hazards involved.

2,4-Dihydroxy-Quinoline - The following charges of this intermediate were used:

Charge	3-4	"as is"
Charge	3-4	recrystallized in the laboratory
"	5-6-7	"as is"
"	5-6-7	recrystallized in the laboratory

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Charge 5-6-7 gave a darker redder product than 3-4 when used "as is" but little difference was found when both were recrystallized. The former appears to be non-uniform since a portion of it contained by analysis only 20% DHQ compared to 37.26% reported for the charge.

The standard method for determining purity of this intermediate is by bromide-bromate titration although coupling with diazotized p-chloro-aniline has been used. The end point in the latter method is not very sharp.

In recrystallizing 2,4-dihydroxy-quinoline a method developed at Jackson Laboratory was followed (Tentative Semi-Works Process for Purification of 2,4-Dihydroxy-Quinoline). An outline of the procedure is given below:

To 750 cc. water at 75-80°C.,
add 100 g. DHQ 100% basis
Stir until dissolved (20-30 minutes)
add 2 g. Nuchar (or Norite)
Stir 10-15 minutes
Clarify and collect the filtrate
Stir the charge until the temperature drops to 20-25°C. Stir at least 1 hour at 20-25°C.
Filter and wash from the container with
24 g. salt dissolved in 135 cc. water.
Press to a firm cake and hold as wet crystals or dry at 120°F.
Yield 78-80 g. DHQ 100% basis

Nickelous chloride ($NiCl_2.6H_2O$) - A technical grade supplied by Harshaw Chemical Company was used. No specifications are at hand but a relatively low content of other metals is obviously required.

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K-13396

FORMULA SHEET

DUPONT

COLOR CODE DATE 11/14/46 NAME Fast Yellow Toner K-2409 (Exp)

OBJECT To make "Lithosol" Fast Yellow 3GD by a straight thru process.

BASED ON Lab. 1235-23A and B

BATCH SIZE-MOLS. 2.0 BATCH No. OF "K" SAMPLE Lab. 1235-23A and B.

LBS. OR GMS.	MATERIAL	100% WT.	GAL.	C. C.	MANIPULATION	N#
			180		of water at 104°F. Add	
182	Muriatic Acid	182			Stir 2-3 minutes. Add	28
260	Para chlor aniline 98-99% purity	255			Stir 15-20 minutes to solution at 104°F. Cool to 40-42°F. with	
900	Ice				approximate volume	57
			300		Add in 10-12 minutes	
140	Sodium nitrite ± 98%	138	60		dissolved in cold water Stir at 50°-60° for 15 minutes test during stirring: CR pos. KI pos. Shut off agitator and allow to settle for 10-15 minutes. Couple	5
			400		of water at 140°F. Add	
338	2:4 dihydroxy quinoline (100% free base)	338			stir to solution in 15-20 minutes at 140°F. Test: BY pos. CY neg.	
64	Soda Ash ± 98%		40		Add dissolved at 140°F.	3
			900		Adjust to at 50°C. with	
1800	Ice				and water	57
					Couple by running the diazo under the surface into the dihydroxyquinoline in 30-40 minutes maintaining temperature at 50-68°F. Regulate rate of addition at end of coupling to avoid excess of diazo. Test BY pos. pH 8.0 - 8.2 diazo neg. with H acid solution DHQ pos. with DCB tetrazo Stir 30-40 minutes after coupling.	
					Heat to 190°-194°F. in 25-35 minutes Add previously prepared solution	
80	Caustic Soda ± 50% solution	80	60		diluted with water Add in 1-2 minutes with stirring	7
120	Acetic Acid ± 80% solution	120			Test: pH 6.5-7.5 Adjust if necessary.	3(

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FORMULA SHEET

Page 2.

COLOR CODE DATE 11/14/46 NAME Fast Yellow Toner K- 2409(Exp.)

OBJECT

BASED ON

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

LBS. OR GMS.	MATERIAL	100% WT.	GAL.	C. C.	MANIPULATION	N#
260	Nickel Chloride Crystals, $NiCl_2 \cdot 6H_2O$		120		Add in 8-12 minutes dissolved at 140-180°F.	
					Caution: Watch for excessive foaming	
					Stir 5-10 minutes Record pH (normal 4.6 - 4.8)	
±50	Caustic Soda ±50% solution	50	30		Then add in 5-10 minutes diluted with cold water	7
					Test: BL-very slight, pH 6.5 - 7.0 Adjust pH if necessary.	
					Hold at 190°-194°F. for 2 hours	
					Test: Adjust pH to 6.5 - 7.0	
					Press, wash, dry according to attached Processing Data Sheet.	

CALCULATED COMPOSITION

Ni complex of PCA-DHQ 100%

STANDARDIZATION

By rubout in V.D.
MT 1:2 XT 1:100 ZnO

PACKAGE 100 LBS. PER I Bbl. COST GROUP SIGNATURE A. D. REIDINGER

GOAL YIELD 655 lbs. "as is" (0.3% H_2O, 652 lbs. anhydrous) N.B. 1235-23.

K-13399

COLOR CODE K2409 NAME Fast Yellow Toner DATE 11-14-46 GOAL YLD. 655#

MAKING

VAT USE	PREFERRED VAT NO.	GAL./IN.	ALTERNATE VATS VAT NO.	GAL./IN.	VAT NO.	GAL./IN.
Diazo Vat	301	20.2				
Coupling Vat	213	71.0	206	71.0		
Strike Vat						

PRESSING

	PREFERRED	
PRESS NUMBER	22	
TYPE PUMP	Steam	
CUBIC FEET PER STANDARD BATCH	74	
FRAMES PER STANDARD BATCH	40 (2")	
TYPE CLOTH	#8 duck	
NUMBER OF CLOTHS PER PLATE	2	
TIME OF FILLING	3-4 hrs.	
TIME OF WASHING	4-5 hrs.	
WASH WATER—TEMPERATURE	City	
WASH WATER—PRESSURE	-	
END POINT	Cl free	
DRY CONTENT OF CAKE	20%	

PRESS WITH WITHOUT AGITATION

SPECIAL CONDITIONS

DRYING

	PREFERRED	
TYPE DRYER	High Velocity	
NUMBER OF CARS	3	
PANS PER CAR	44	
TIME OF DRYING	+ 24 hrs.	
TEMPERATURE OF DRYING (DRY BULB)	176°F.	
WET BULB TEMPERATURE		
HUMIDITY OF DRYING		
TEST FOR DRYNESS		

SPECIAL CONDITIONS

GRINDING

	PREFERRED	
NUMBER OF GRINDER	24" Mikro	
MILL SPEED	1750 RPM	
HAMMER TYPE	Stirrup	
SCREEN	1/16"	
FEED SPEED	-	
MINUTES PER BARREL	-	
FINENESS SPEC.	-	
DRY ICE	-	
POUNDS PER PACKAGE	100#	
PACKAGE TYPE	1Bbl.	
LINER TYPE		

SPECIAL CONDITIONS Avoid overheating during pulverization. Color is ignited by sparks at temp. of 200-250°C. Non-bleeding color. Avoid contamination.

REMARKS:

SIGNATURE A. D. Reidinger

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NOTES FOR K-2409

K-2409 is a modification of the Chambers Works process for Lithosol Fast Yellow 3GD our YT-562-D, and differs from the latter in the details discussed below.

1. Clarification of p-chloro-aniline and of the dihydroxy-quinoline solution is omitted. Both of these changes are dependent on quality of intermediates used.

2. The coupled dye is not isolated but is carried straight thru to the metallization stage. In general this had the effect of producing darker masstones but when DHQ of good quality was used the difference was considered to be of tolerable degree.

3. The amount of sodium carbonate in the coupling was reduced to 60% of that used in the original formula. This lessens to some extent the foaming which occurs during addition of the nickel-chloride but it also tends to slow the rate of coupling slightly. When less than the K-2409 amount of alkali was used, a trend to darker and weaker products was noted.

4. Neutralization was effected by addition of all the caustic soda at once instead of in several portions at half hour intervals as previously. It is considered advisable to avoid addition of excess NaOH although adjustments from pH 7.4 to 7.0 have been made without adverse effect. Final pH below 6.0 results in lower yields.

5. The development period was reduced from 3 to 2 hours. A shorter period, e.g. one-half hour, may be possible but was not considered safe because of the slightly lighter masstone obtained, which could be indicative of incomplete development.

The product obtained in the laboratory on K-2409 was darker than the present YT-562-D standard but slightly stronger and more intense in tint; lightfastness and other properties appear to be equal.

Goal Yield was 655 lbs. "as is" (0.3% water, 652 lbs. anhydrous).

NOTE:

p-Chloro-aniline is extremely toxic and special care should be taken to avoid contact with the skin or inhalation of dust. At present it is received in solidified condition in drums from which it is removed by breaking it into lumps. It is recommended that this be done out of doors or in a room where other people are not working.

A. D. REIDINGER
11-14-46

ADR:CC

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