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NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

"MONASTRAL" GREEN GX, SEMI-WORKS STUDY

Period Covered

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Final Report

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INTRODUCTION:

A direct process for the preparation of a [illegible] pigmentary CPC Green (designated Green GK), which requires no mechanical [illegible] size reduction, was developed in the laboratory (Report MR-5[illegible]-7). This process appeared attractive both from the standpoint of manufacturing cost and tinctorial properties compared with solvent-milled Green. Therefore, a Semi-works study was undertaken to develop scale-up information and procedures for the commercial production of "Monastral" Green GK.

SUMMARY & CONCLUSIONS:

A laboratory Green GK process, known as "Green 25", was scaled up from laboratory to plant using data and techniques developed in #14 Bldg. Semi-works. However, the product was found to be excessively harsh in texture and could not be ground on a roller mill. To overcome this deficiency, a simplified process, "Green 70", was developed by the laboratory.

Semi-works study of the "Green 70" process was concerned mainly with obtaining scale-up information and pin-pointing production difficulties. The major scale-up problem encountered was the excessive foaming of sodium stearate during the ortho-dichlorobenzene steam distillation step. A water spray, used in combination with a foam modifying agent and a distillate vapor entrainment separator, was found to be effective in controlling the foam. Operating data obtained in the Semi-works permitted the successful reduction to practice of the "Monastral" Green GK process in the plant.

DISCUSSION OF RESULTS

A. "GREEN 25" (see Fig. 1)

1. Preparation of ODCB Granules:

A 1:1 ($AlCl_3$/CPC) rotary drier crude made in the Newport Plant, was used for the Semi-works study of the "Green 25" process.

To make the ODCB granules, the rotary drier Green Crude was drowned in water (1#/gal.), granulated by the slow addition of ODCB (.65#/#pigment) to the agitated slurry, and the granules isolated by filter pressing and washing.

Following the drowning, aqueous extraction at the boil for one hour was found to be advantageous over cold drowning alone for best tinctorial properties.

Variation of the ODCB granulation rate was not studied, but vigorous agitation was found to yield finer grains. Filter pressing of the ODCB granules was possible, although frequent pluggage of the pump lines, and frame fill ports was encountered. A press volume of 0.038 ft^3/# pigment is necessary for this step. The use of cotton twill filter cloth[1] permitted rapid filtration rates and thus decreased the tendency for line pluggage. Water dilution of

1 Turner Halsey #3628

the filter feed was also beneficial in this respect. Since weight ratios of ODCB/color above 0.65/1 gave enhanced quality, but granules of sticky consistency, a modified process, wherein part of the ODCB is added in the still, was preferred for ease of granule handling.

Impurities must be removed from the granules before steam distillation to avoid "blooming" in the final product. This was accomplished by vat or press washing. Press washing is the more attractive, as less manipulation and wash water is required. Although elaborate washing is not essential, the washing should be carried to a wash filtrate pH of 5 or above to insure desired product quality.

2. Distillation of the Granules:

The first problem encountered in the distillation of granules was pellet formation. Laboratory results indicated that rapid steaming reduced the tendency toward pellet formation. However, plant experience showed the opposite trend. High ratios of ODCB to pigment (>.85/1) and rapid steaming tended to promote the formation of pellets. The use of "Triton X-100" or of sodium stearate as a surface active agent in the steam distillation eliminated pellet formation. Steam rates of 2# steam/hr./# pigment or less yielded pellet free products.

The rate of ODCB removal during steam distillation of the granules was found to be a function of time and granule size only, and not rate of steam input. Analysis of ODCB removal rate data indicated that desorption of ODCB from the granules occurs. A typical ODCB granule distillate curve is shown in Figure 3.

Additional ODCB treatment, obtained by refluxing 0.65/1 granules and also by further granulation with an additional 0.20 parts ODCB/part pigment prior to distillation yielded more intense and stronger products.

Improvement in tinctorial properties of the product resulted from increased pH during distillation. Di-sodium phosphate, tri-sodium phosphate, and sodium hydroxide were used. Best results were obtained when a pH of 11 or above was employed in the still charge.

3. Isolation of Final Product:

The shell of the ODCB granule persisted through the distillation. Therefore, handling and processing difficulties were encountered in pumping, filtering, and washing the distillation product. Thus, a hard settling sandy product resulted. Residual ODCB and acidity were noticeable in the product grains either after standing as a pulp or wet crushing or milling.

A slow soft settling pulp can be made from distilled granules by colloid milling. Slower settling pulps were produced at closer mill settings, but product rubout strength loss resulted when the color was milled at less than 0.010 inch mill clearance.

Sodium stearate (2% on pigment) was also found to disperse the granules effectively during distillation, yielding a smooth slow settling pulp which does not contain residual ODCB or acidity.

4. Pigment Texture:

Hard sandy granule shells remain after distillation. The dry, pulverized pigment exhibits a harsh texture, which renders the product unacceptable in ease of grinding on a roller mill, particularly with respect to rate of strength development, grit elimination, and in general mill behavior.

High speed pulverization of the dried product, wet pulverization, colloid milling, colloid milling plus homogenization, and acetone extraction of the pulp did not improve the texture. Alkaline extraction of colloid milled pulp gave some improvement. The use of sodium stearate as a detergent and dispersing agent during granule distillation gave an improved textured product equal to GT-674-D, SD 121. With the advent of the new "70" process (see Fig. 2) developed in the laboratory, granule handling was eliminated and products of superior texture properties compared with current green GT-674-D, SD 121, resulted. Therefore, development work on the "Green 25" type processes was discontinued.

B. "GREEN 70"

1. Crude Extraction:

In the "70" process (Fig. 2) rotary drier Green Crude drowning was performed in the same manner as in the "25" process, except that the ODCB granulation was omitted at this point. Initially, crude Green GX was drowned in water (1#/gal.) and extracted for 2 hours at 90-95 C. It was found that a 1 hour extraction without heating was sufficient to obtain good quality and disintegrate all the lumps of crude.

The extracted crude must be filtered and washed to remove impurities which cause "blooming", although only slight quality differences were noted by varnish dryer rubout. A press volume of 0.0244 cu. ft./# pigment is required for this operation.

Crude GX should be washed to a filtrate pH of 4.5 or above (equivalent to ca. 4000 ohms at Newport).

2. Alkaline Extraction:

The original laboratory process required that the extracted crude be boiled in caustic (0.67#/# color) for one hour at a slurry concentration of 1# color/gallon. Semi-works study of this operation showed that identical results were obtained by extracting with 0.07# caustic/# color at room temperature for 15 minutes. Inferior quality resulted when lower amounts of caustic were used.

3. Granulation:

ODCB granulation is performed in the steam distillation vessel under well agitated conditions using the alkaline extracted slurry. Early work was performed using an ODCB addition rate of 0.55# ODCB/# pigment/hr. This rate was later increased to 5.0# ODCB/# pigment/hr. without adverse effect upon product quality.

Varying granulation temperatures up to 90° C. did not affect product quality. The addition of sodium stearate before granulation yielded a product of inferior quality.

Finer ODCB granules result from the "70" process compared to the "25" process, presumably because the extracted crude is better dispersed in alkaline media.

Results of duplicate Semi-works runs showed the use of .75 lbs. ODCB/lb. color yielded slightly weaker products, whereas the use of 0.85# ODCB/# color or more gave products of strength equal to GT-674-D standard. Masstone becomes lighter with increased ODCB contact time.

ODCB recovered from the steam distillation may be reused with no adverse effect on quality.

4. Distillation:

After the ODCB granulation step, stearic acid (3% on the weight of the color) and sodium nitrite (2% on the weight of the color) are added. The ODCB steam distillation is then commenced using both jacket and live sparger steam.

a. Foaming

In the initial Semi-works trials, sodium stearate, required for quality reasons, caused extreme foaming during distillation, and a very slow distillation rate resulted. To obtain a practicable process, the following methods of foam suppression were investigated: (1) variation of pH, sodium stearate concentration, and addition of electrolytes; (2) substitution of non-foaming detergents for sodium stearate; (3) addition of anti-foam agents; and (4) mechanical methods.

It was found possible to reduce the foaming tendency by lowering pH; but inferior quality resulted. Lower amounts of sodium stearate yielded progressively poorer pigment quality, with no apparent decrease in foaming. The addition of an electrolyte, NaCl, in sufficient quantity to eliminate foam, yielded a weak product.

The results of the non-foaming and anti-foam agent study are tabulated in Tables 1 & 2. Tri-cresyl phosphate was found to be effective by rendering the foam light and fragile. Since tri-cresyl phosphate hydrolyzes in boiling caustic, it should be replenished every 1-1/2 hours during distillation. Other anti-foam agents were also found to be effective, but poor pigment quality resulted.

Some promising leads resulted from the study of non-foaming detergents. These were not pursued, as satisfactory mechanical means for foam handling had been discovered.

Mechanically, the foam can be checked by a high velocity, flat, fish-tail water spray directed downward on to the surface of the still slurry. Foam is moved by the still agitation under the spray, and is thus maintained at a low level in the still. A "Sprayco"[1] model #0.031F spray was used in the Semi-works, and a constant still liquid level maintained by proper adjustment of jacket steam. Since a fine mist of still slurry is entrained in the vapor escaping from the foam surface, a 6 inch thick "Yorkmesh"[2] knitted wire demister was used to remove this entrainment. Failure to remove entrainment would result in poor yield of color. Also, ODCB recovery would be low since the distillate is emulsified in the presence of sodium stearate. In addition, pluggage of the condenser might be encountered.

b) pH:

Finished product quality was found to deteriorate progressively with decreasing pH below 10.0. This degradation is further aggravated by contact with carbon or stainless steel used in plant and Semi-works equipment. Therefore, caustic solution should be introduced into the still prior to the addition of the crude.

c) Rate:

The rate of ODCB distillation in the "Green 25" process appeared to be controlled by desorption from granules and not rate of steam input. In the "Green 70" process, however, the rate of ODCB removal was found to be proportional to the steam throughput. It is postulated that the ODCB granule formed in the "70" process is of sufficient fineness to allow rapid ODCB desorption. A typical distillation curve is shown in Figure 3. The ODCB removal rate is limited by foam formation. Distillation rates as high as 0.078 gallons of distillate/min./square foot of still surface were used before excessive foaming was encountered.

1. T.M. Spray Engineering Co., 114 Central St., Somerville 45, Mass.
2. T.M. Otto H. York Co., 69 Glenwood Place, East Orange, N. J.

d) End Point:

The Semi-works distillation is terminated when an ODCB layer is no longer noticeable in 500 cc. of distillate. Due to a more complex arrangement of vapor piping in the plant, an end point of less than 20 cc. ODCB/500 cc. of distillate is adequate.

5. Isolation of the Final Product

Upon completion of the steam distillation, the color is pressed, washed, and reslurried to yield a standard pulp (N-764). Early plant washing difficulties prompted Semi-works study of this step. It was found that steam distilled color was easily "packed" into the press if insufficient press volume is employed. Then extremely slow and poor washing results. 0.028 to 0.035 ft.^{3}/# color was found to be a satisfactory press loading volume. The tinctorial properties of the finished product were not affected by the extent of washing. However, the finished Green GK should be hot water washed to a filtrate resistance of 2500 ohms to insure removal of a major portion of the soluble salts.

Physically, the "Green 70" slurry (N-764) has more desirable settling characteristics, being smooth, soft and slow settling compared with N-624 or "Green 25" pulp.

A 12-inch Shriver thickener was evaluated and found to be capable of filtering the still slurry, washing the pulp, and yielding a pumpable pulp of 25% solids content. Since repulping and manual handling would be eliminated, the Shriver thickener should be considered in any addition to or replacement of N-764 isolation equipment.

6. Process Yields

Yields obtained in the Semi-works are shown below. Chlorination yields are reported elsewhere.

Step	Yield	Basis
Crude extraction	99.3%	Lab. analysis
Steam distillation	94.3%	Commodity
Steam distillation	98.6%	100% CPC

The steam distillation yields are based upon the use of extracted crude.

Semi-works recovery of ODCB averaged 90%.

REFERENCES

1. Notebook 1461
2. Reports KN-54-7 and KN-54-8

NOTES ON RAW MATERIALS

1. Rotary dryer crude - ex Newport Plant
2. Ortho-dichlorobenzene - technical grade ex Solvay or Dow
3. Sodium nitrite - N-5 (Newark Plant)
4. Caustic - equal to N-721 (Newark Plant)
5. Stearic acid - "Neo-Fat 18-53" ex Armour
6. Tri-cresyl phosphate - ex Montrose Chemical

APPENDIX I

S.W. PROCESS - GREEN GX COLD EXTRACTION

EQUIPMENT: 8 Vat and 202 Press

1. Put wood plug in outlet 8 Vat.
2. Add 20" water = 350 gallons.
3. Add rotary drier crude equal to 265# color. Wear gas mask.
4. Stir 1 hour.
5. Filter in 22 frames - 202 Press.
6. Wash Cl^- free - use 140°F. water. pH should be 4.0 or above; less than 3 grains/gallon.
7. Dump press and place pulp in 55 gallon drum - obtain dry content.

APPENDIX XX

S.W. PROCESS - STEAM DISTILLATION AND PRODUCT ISOLATION

EQUIPMENT: 1. 29 Tank, complete with 0.031F Sprayco spray and 4" x 6" diameter York demister.

2. Old wood press, 18", 0.125 $ft.^3$/frame

1. Add 6" water in 29 Tank - turn on agitator.
2. Add Green GX water extracted presscake Lot ________ ________ lbs. = 35# dry.
3. Make volume to 10 inches with water.
4. Add flake caustic (N-721) - stir 15 minutes.
5. Add uniformly in 10 minutes - 30# ODCB.
6. Record pH ______.
7. Add 320 grams sodium nitrite (N-5).
8. Add 477 grams stearic acid (Neo-Fat 18-53)
9. Add tri-cresyl phosphate - 10 cc.
10. Seal steam still. Turn on water spray to 20-30 psi and start distillation.
11. Add 10 cc. tri-cresyl phosphate during distillation at 1 hour intervals.
12. Stop distillation when no separate layer of ODCB is found in 500 cc. of distillate.
13. Record final pH _____, final volume _____in. #ODCB recovered _____lb. and # water condensed _____lb.
14. Filter slurry from 29 Tank in 10 frames, old wood press - use 29 Tank pump Record pressure ______psi Time start ______ Time finish ________
15. Wash with 140°F. water to less than 3 grains/gal.
16. Dump press record condition of cakes _______ wt. p.c. _____ lb. dry content _______% yield dry _______lb.

TABLE I

NON-FOAMING DETERGENTS

In Order of Increasing Tendency to Foam

Detergent*	Source**	V.D. Rubout Compared With Stearic Acid Product: Strength	Masstone
K-Wood Rosin	N-239 (Newark)	=	dk.
"All"	Grocery shelf	=	dk.
Armine 2HT	Armour	weak	- - -
Stearox CD	DX 2395	s. weak	- - -
Ahcowet RS	DX 2188	s. weak	dk.
Armid "O"	Armour	vs weak	dk.
Stearox AJ	Monsanto	weak	- - -
Daxad 11	DX 1646	v. weak	- - -
Na Lignin Sulfonate	DX 1772	v. weak	- - -
Brij 30	Atlas	weak	dk.
Brij 35	Atlas	s. weak	dk.
Stearic Acid + Tri-sodium phosphate	- - -	vs weak	=
Stearic Acid + Na Pyro phosphate	- - -	=	=
Peg 300 Mono Stearate	DX 2913	s. weak	——
Peg 200 Mono Laurate	DX 2895	vs weak	——
Peg 300 Di-Laurate	DX 2907	vs weak	——
Stearic Acid Neo-Fat 18-53	Armour	=	=

*Amount used was 3% by weight, based on color.

**DX numbers are Experimental Station file numbers.

TABLE II

ANTI-FOAM AGENTS

In Order of Increasing Foaming Tendency

Pre - 500 ppm Based on Slurry

Agent	Source*	Product Strength by V.D. [illegible] vs. No Agent**
XP-6450	DX 1746	weak
Tri-cresyl phosphate	Montrose Chem.	"
Tri-butyl phosphate	DX 2986	"
Defoamit	DX 2177	N.E.
Na Lignin Sulfonate	DX 1772	weak
Surfax WO	E. F. Houghton	"
Paper Pulp Defoamer	DX 2108	N.E.
D.C. Anti-Foam "A" Emulsion	Dow Corning	"
D.C. Anti-Foam "A" dissolved in Xylene	Dow Corning	"
D.C. Anti-Foam "A"	Dow Corning	"
Dealvac 506	E. F. Houghton	very weak
Emulsimate [illegible]	E. F. Houghton	N.E.
Seamaline 550	E. F. Houghton	N.E.
Nothing		---
Stabron 970	E. F. Houghton	N.E.
Dealvac 311	E. F. Houghton	N.E.
Foamex	Glyco Products	N.E.
Span 20	Atlas	N.E.
Pine Oil	X-757 (Newark)	N.E.
Turkey Red Oil	X-75 (Newark)	N.E.
Octanol-1	X-503 (Newark)	N.E.
Bubble Breaker	Balck	N.E.
Foamrex	Socony Vacuum	N.E.
Raw Linseed Oil	Sales Service	N.E.

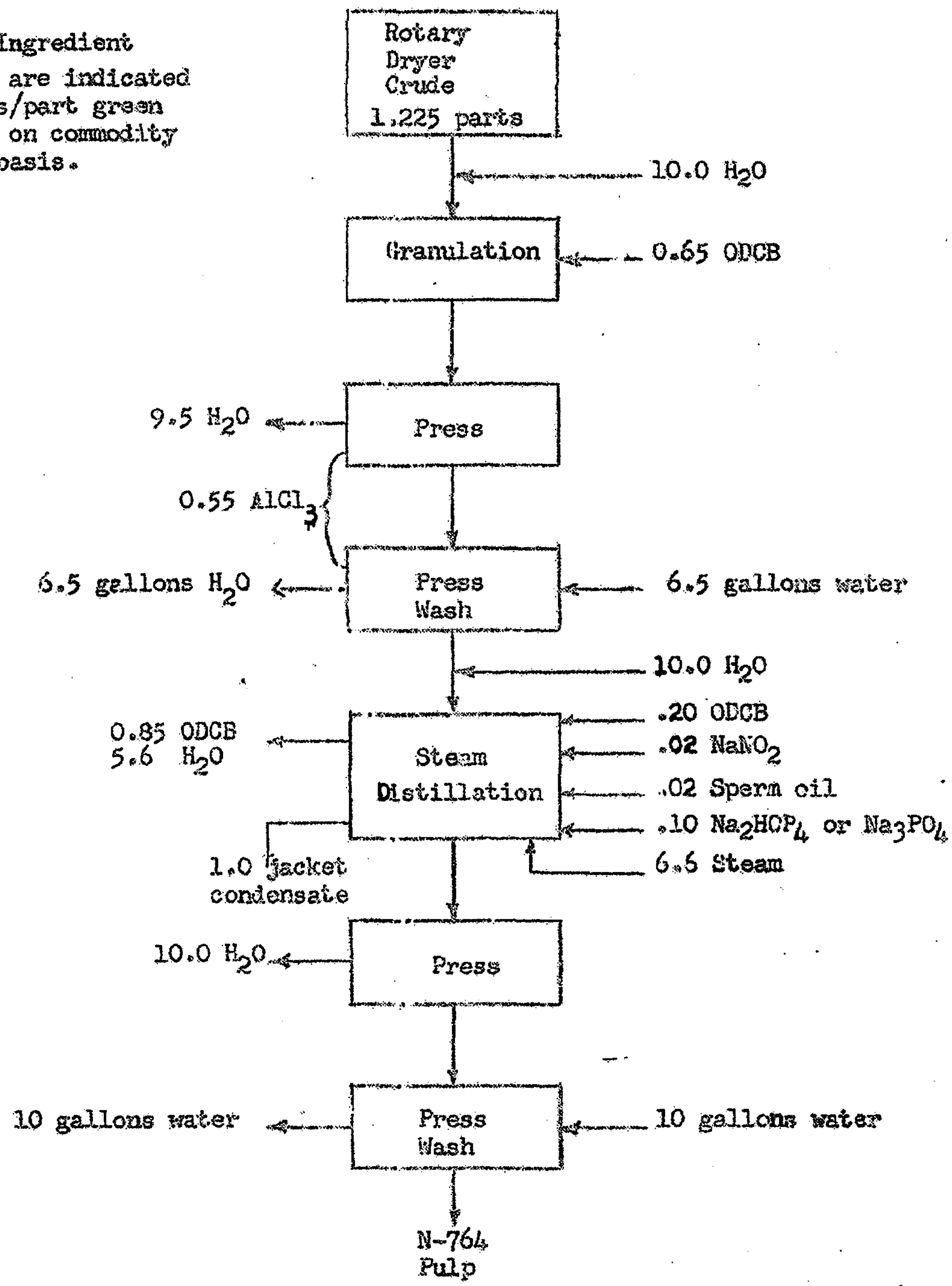
*DX numbers are Experimental Station File numbers

**N.E. - Not Evaluated

Fig. 1

"GREEN 25"

NOTE: Ingredient amounts are indicated as parts/part green pigment on commodity weight basis.



PROJ. TITLE GREEN GX	SIGNATURE:
SUBJECT: "GREEN 25" FLOW SHEET	PROJ. NO. A/C NO. 29856

DIVISION E.S.D.	PLANT NEWARK COLORS RESEARCH	DATE 11/15/54	NO.

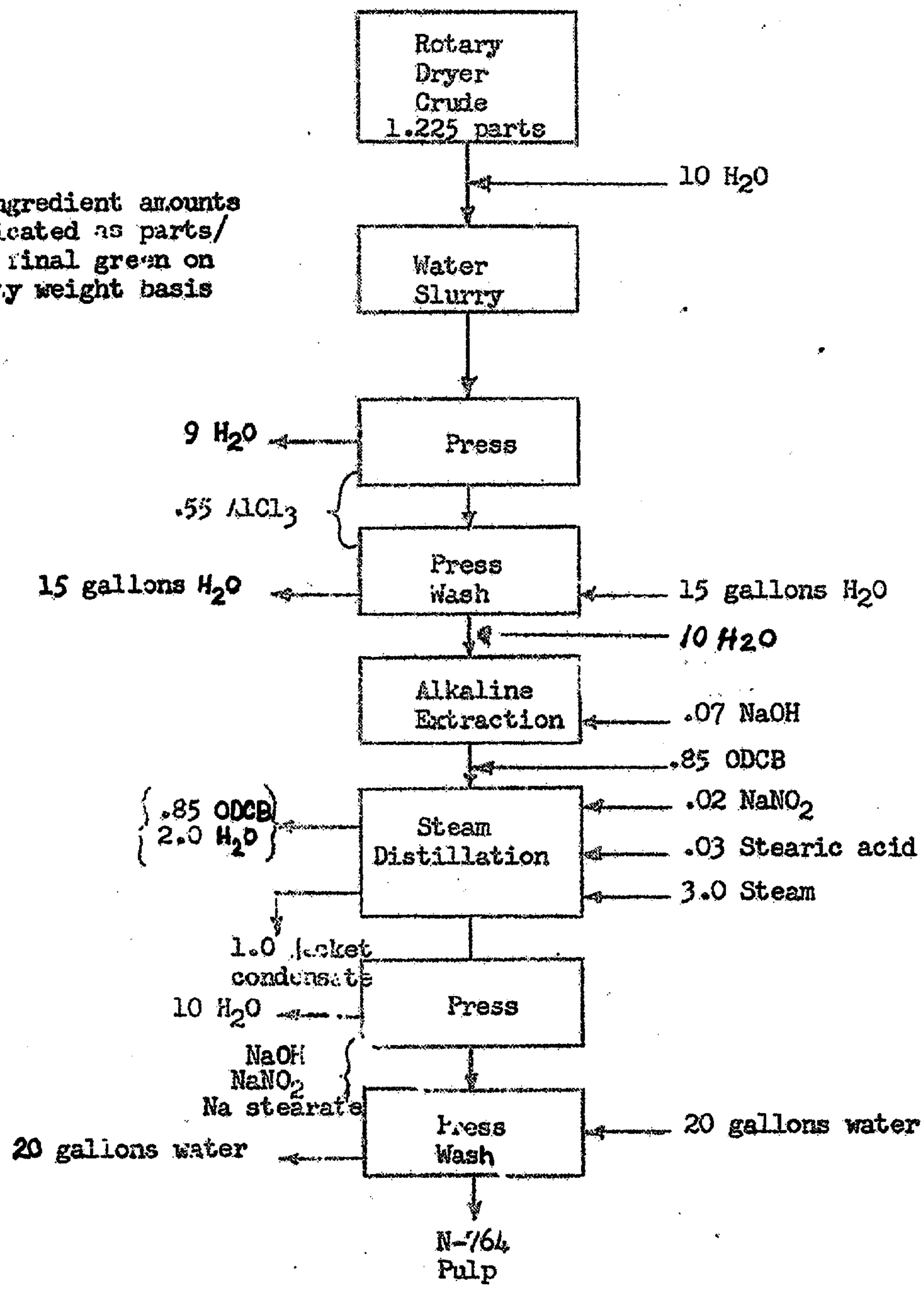
EN-3051-B

ENGINEERING DEPT. E. I. DU PONT DE NEMOURS & CO. (INC.)

Fig. 2

"GREEN 70"

NOTE: Ingredient amounts are indicated as parts/ part of final green on commodity weight basis



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SUBJECT: "GREEN 70" FLOW SHEET		PROJ. NO. A/C NO. 29856
DIVISION E.S.D.	PLANT NEWARK COLORS RESEARCH	DATE 11/15/54 NO.

DUP050070028

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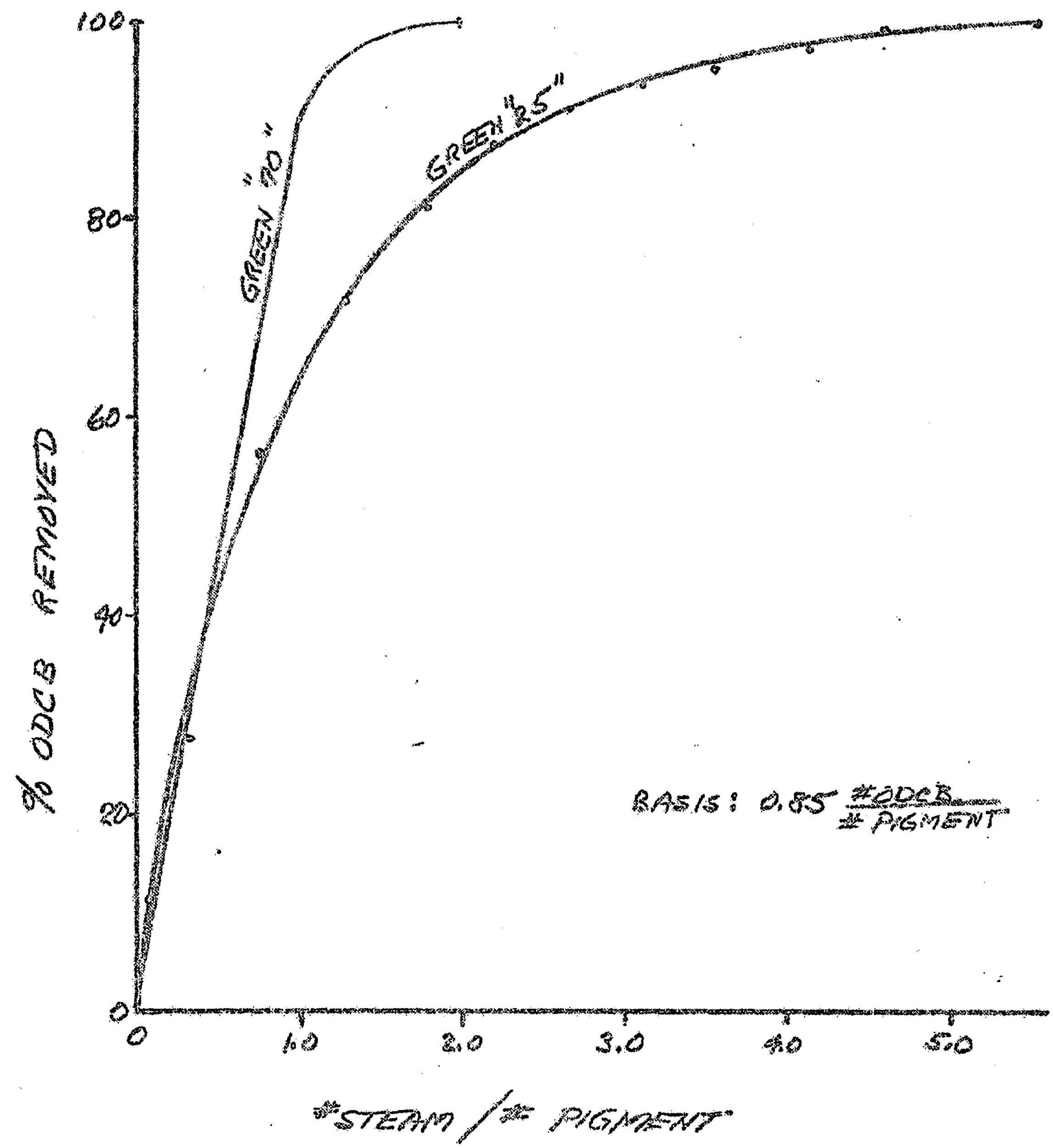
ENGINEERING DEPT. E. I. DU PONT DE NEMOURS & CO. (INC.)

FIG. 3



PROJ. TITLE GREEN GX		SIGNATURE:	
SUBJECT: ODCB STEAM DISTILLATION		PROJ. NO. A/C NO. 29856	
DIVISION E3D	PLANT NEWARK COLORS RESEARCH	DATE 9/20/54	NO.

DUP050070029