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Newport, Delaware
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MR. V. H. CHALUPSKI
NEWPORT -

GREEN GX - "70 PROCESS"

Submitted herewith are sample operating forms for manufacture of Green GX in the existing plant equipment as modified for "interim" production of this material. Also included are operating notes and data collected during the plant manufacture of Green GX in two campaigns of roughly 10,000 lbs. and 15,000 lbs. respectively.

Selection of material for standardization has been completed at Newark, and agreement reached with Sales that the change over from solvent milled to GX green can be made when the plant is ready.

The Chemical Division completed its plant development work during the last campaign; therefore, it is requested that the Production Division assume responsibility for future plant manufacture of Green GX.

E. F. Klenke, Jr.

E. F. KLENKE, JR.
CHEMICAL DIVISION

EFKJr:ad

Attach.

Form - 13

CRUDE GREEN "GX"
CHLORINATION AND DRYING

Autoclave-201-A, 201-B Dryer 213-A, 213-B Cl No._____

Date	Time	Opr.	Instructions	Record	Quantity Std.	Quantity Used
			1. Check autoclave-MT bottom valves closed			
			2. Start addition of sulfur chloride-record % Cl	____%	68.0-69.0	
			3. Finish addition of sulfur chloride(final temp. in 201, 30°C or lower)		3400#	____#
			4. Finish addition of CF crude			
			Lot_____Lbs._____		268#	____#
			Lot_____Lbs._____			
			Lot_____Lbs._____			
			5. Finish addition of copper chloride (anhyd.)		27#	____#
			6. Finish addition of Ohio Apex Alum. Chl.		268#	____#
			7. Finish bolting head on autoclave			
			8. Check operation of automatic valve. Set at 100 psi			
			9. Heat charge to 50°C with 65°-68°Chot water		20 min.	____
			10. At 50°C shut off hot water and allow temp. to rise to 65°-70°C reaction temp. When reaction starts, put cold water on jacket			
			11. When venting OK at 100 psi, reset controller to 200 psi, then to 265. After pressure is under control at 265 psi, start steam to autoclave jacket and heat to 175°C			
			12. Start of 4 hrs. holding period at 175°C min. and 265 psig min. Record max.temp.	____°C		
			13. End of holding period at 175°C; Pressure _____	____hrs	4 hrs.	
			14. Pressure vented to	____psi	100 psi	
			15. Charge cooled to	____°C	130°C	
			16. Vent pressure to 30 psi	____psi	30 psi	
			17. Dump into rotary dryer-salt (Sodium Chlor)		300#	____#
			18. Drop charge from autoclave to rotary dryer			
			19. Allow 15 min. for charge to drop, then add sulfur chloride flush to autoclave		500#	____#
			20. Finish dropping flush to rotary dryer			
			21. F.B. and back-up valve closed--autoclave MT or heel	_____		
			22. Start steam to rotary dryer jacket (roughly 1/8 turn open)			
			23. When vapor temp. reaches 70°C--start chlorine to dryer at minimum rate to hold float suspended (about 50-75#/hr.)			
			24. Heat dryer from 70°C to 130°C in 1-1/2 hrs.	____hrs.	1-1/2 hrs.	
			25. When absorber temperature peaks, open jacket steam valve wide.			
			26. When vapor temperature drops to 110°C (from ±130°C) start chlorine to dryer at 100#/hr. for 3-1/2 hrs.	____hrs	3-1/2hrs.	
			27. Finish chlorine addition			
			28. Start CO_2 flush--leave steam on		1/2 hr.	

(over)

Date	Time	Opr.	Instructions	Record	Quantity Std.	Quantity Use
			29. Start cooling water to dryer jacket			
			30. Total hrs. dried.	____hrs.		
			31. Start discharging crude from dryer			
			32. Finish discharging crude from dryer			
			33. Record pigment weight--take 2 quart sample	____#		
			34. If drummed use polythene lined drums & lids (lining must be in very good condition)			
			35. Stencil lot no. and weights on drums--Record drum weights			
			Drum #1--Net weight	____#		
			#2-- " "	____#		
			#3-- " "	____#		
			Total Weight	____#		

GREEN GX FINISHING N-764

(Extraction-Distillation-Finishing)

Batch Size - 1000# Crude Extr. - 219 tk.

Press - 235 Still - 225 Cl No._____

Press - 241 Mixer - 249 Cl No._____

Date	Time	Opr.	Instructions	Record	Quantity Std.	Quantity Used
			1. Check 219 tank--should be empty			
			2. Add water to 219 tank	"	30"	XXXXXX
			3. Dump into 219 tank-G-	#	1140#	XXXXXX
			4. Start 219 tank agitator and stir for 2 hours	hrs.	2 hrs.	XXXXXX
			5. Pump the charge from 219 tank to 235 press(use 31 frames)-Run ALL press filtrate to 237 tank. Do Not start press washing			
			6. Add water to 219 tank	"	30"	XXXXXX
			7. Dump into 219 tank-G-	#	1140#	XXXXXX
			8. Start 219 tank agitator & stir for 2 hours	hrs.	2 hrs.	XXXXXX
			9. Pump charge to 235 press--run all press filtrate to 237 tank			
			10. Flush 219 tank empty			
			11. Start 235 press washing, use 40°C water Run bleeding spigots to 237 tank			
			12. Wash for 8 hrs.; sample every 2 hrs.	hrs.	8 hrs.	XXXXXX
			and record ohms-- Start			
			2 hrs.			
			Record 4 hrs.			
			Ohms 6 hrs.			
			8 hrs.			
			13. Pump filtrate from 237 tank to 244 press--during 235 press washing cycle			
			14. Check 237 tank--pump all the filtrate to 244 press--flush clean			
			15. Add water to 237 tank	"	20"	XXXXXX
			16. Start 237 tank agitator			
			17. Drop 235 press charge into 237 tank			
			18. Record final volume in 237 tank	"	XXXXX	XXXXXX
			19. Check 225 still--must be empty. Do not bolt lid.			
			20. Pump charge from 237 tank to 225 still			
			21. Flush 237 tank empty--watch volume in 225 still--45" max.--by gauge			
			22. Record final volume in 225 still	"	45"Max.	XXXXXX
			23. Close lid & start still agitator			
			24. Add to 225 still--50% caustic-50"	XXXXXX	140#	"
			25. Agitate for 10 minutes--check pH	pH	pH 10 min.	XXXXXX
			26. Add ODCB - Meter-Before _____	XXXXXX	XXXXXXXX	XXXXXX
			After _____	XXXXXX	XXXXXXXX	XXXXXX
			Added _____	XXXXXX	78 gal.	gal
			27. Open lid with agitator on, then add:			
			Stearic acid	XXXXXX	30#	#
			Sodium Nitrite	XXXXXX	20#	#
			Tri Cresyl Phosphate (Celluflex)	XXXXXX	1-1/4#	#
			28. Check water spray			

(over)

GREEN GX FINISHING

Cl No. _____
Cl No. _____

Date	Time	Opr.	Instructions	Record	Quantity Std.	Quantity Used
			29. Close lid, and bolt turn water on ODCB cond.			
			30. Open jacket steam valve 2 turns (no sparger steam).			
			31. When still body temp. reaches 77°C, close large jacket valve and use by-pass valve.			
			32. Start water to still spray nozzle (adjust to 5# below inlet pressure)			
			33. Regulate jacket by-pass valve to keep still temp. at 96+°C., but do not go above 15" still pressure.			
			34. Add 1 qt of Tri Cresyl phosphate (Celluflex) to 225 still 2 hrs. and 4 hrs. after temp. reaches 96°C			
			2 hr. addition	XXXXXXX	1 qt.	____ g
			4 hr. addition	XXXXXXX	1 qt.	____ g
			35. Record distillation data every 30 min. on attached sheet			
			36. When distillate samples show 20cc ODCB in 500cc total sample, continue for 15 min. more, then resample. If the resample is the same the distillation is completed. Check by smelling vapor from sample nozzle in vapor line.			
			37. Turn steam off--leave agitator on			
			38. Check 241 press--should be empty & clean--set up 22 frames			
			39. Start pressing to 241 press (keep pressure below 20#/sq. in.) Run ALL filtrate to 231 tank.			
			40. Finish pressing			
			41. Start press washing--run all bleeding spigots to 231 tank--sample filtrate every 2 hrs: Record pH and ohms at-Start	_____		
			2 hrs.	_____		
			4 hrs.	_____		
			6 hrs.	_____		
			8 hrs.	_____		
			10 hrs.	_____		
			Wash to 2500 ohms or 6 hrs. minimum	XXXXXX	2500ohms	
			42. Pump filtrate from 231 tank to 244 press during 241 washing cycle(preferably during 235 wash cycle)			
			43. Check ribbon mixer--should be empty, if not, flush it to 231 tank.			
			44. Dump press to ribbon mixer.			
			45. Presscake--Full (yes, no) Firm. Sloppy record no. of empty frames	_____		

GREEN GX FINISHING

Cl No.________________
Cl No.________________

Date	Time	Opr.	Instructions	Record	Quantity Std.	Quantity Use
			46. If necessary, add water to mixer. Mix 1 hour minimum	gal.	XXXXX	XXXXX
			47. Recirculate last 1/4 hour of mixing			
			48. Start drumming from mixer--record pH	pH	XXXXX	XXXXX
			49. Packed drums. N-764 Lot		XXXXX	XXXXX
			50. Pack lot sample taken			
			51. Pump mixer flushes to 231 tank			

GX DISTILLATION DATA

Date	Time	Opr.	Still			Condensate		Steam
			Temp.	Pressure	Level (in)	GPM	ODCB/water	

OPERATING NOTES

The following is a condensation of the data in the summaries of the December 1953 and March 1954 campaigns and includes information that will be covered in more detail in a future report covering plant development of the "70 process."

A - Chlorination

1 - Standard batch size used to date--268# "as is" CF blue, 268# $AlCl_3$, 3400# S_xCl_x, 30# $CuCl_2$. One batch was made using 300# of CF crude and $AlCl_3$, 30# $CuCl_2$ and 3400# S_xCl_x. No operating difficulties were encountered at either batch size; a further increase in batch size should be possible.

2 - Sulfur chloride, with % chlorine in the range 68.0-69.0, produced satisfactory quality material. In general the charges came up to pressure and temperature more rapidly than standard type green (Sb_2O_3 catalyst); however, there was no significant difficulty controlling pressure.

3 - Three chlorinations were made in which the standard quantity (13-1/2#)of Sb_2O_3 catalyst was used in the autoclave, and the 268# of $AlCl_3$ was added to the rotary dryer before the autoclave charge was dropped. This produced dark masstone, blue tint material by GX processing.

4 - Ohio Apex anhydrous $AlCl_3$ was adopted as standard after laboratory and some plant trials of other grades. Quality deficiencies and/or operating difficulties were attributed to the other types of catalyst tried.

B - Drying

1 - Early rotary dryer problems such as extended drying cycles, caked charges, damage to dryer by excessive bar movement, etc. were largely overcome by adding 300# salt (NaCl) to the dryer prior to dropping the charge from the autoclave. The use of lesser amounts (200 or 100 lbs.) did not give any significant improvement; 400# should be tried in the future to determine if additional improvement in dryer performance can be gained.

2 - A controlled rate of heat-up, plus early addition of chlorine (see batch card), were found to reduce the over-all dryer cycle.

C - Extraction

1 - Extraction at elevated temperature was found to be unnecessary. Several batches of satisfactory quality material were produced by merely dumping the crude into water and agitating without adding any steam. The heat resulting from hydrolysis of the $AlCl_3$ raised the temperature to approximately 50°C.

2 - The only limit to the ratio of water to crude is the pumpability of the extracted slurry. The formula quantities worked satisfactorily.

D - Crude Filtration

1 - The ratio of 33# of crude (water extracted basis; or 74# on "as is basis) per cubic foot of 235 press volume worked well for the two long plant campaigns. In general the cakes were good, and satisfactory press filling and washing cycles were attained (see March 1954 summary). Should this step be a production bottleneck, washing cycles of 4-6 hours should be tried.

2 - The only factors limiting the volume of reslurried presscake are pumpability and a volume limit in the still.

E - Distillation

1 - The original process called for the use of 0.65 lbs. 100% NaOH per 1.0 lb. CPC*, with a subsequent 1 hour stir period at 90°C, followed by the addition of 1.0 lbs. orthodichlorbenzene per 1.0 lb. of CPC* (over 1-1/2 hour period). This was ultimately simplified to the use of 0.07 lbs. 100% NaOH/1.0 lb. CPC*, with a subsequent 10 minute stir at room temperature, followed by the addition of 0.85 lbs. ODCB/1.0 lb. CPC* over a ±15 minute period. There was no noticeable change in quality attributable to these changes.

The still slurry must be alkaline (pH 10.0-12.0) at the start of distillation or serious weakness and dullness will occur.

2 - The sequence of addition of the ingredients indicated in the attached formula was established for optimum quality.

*Water extracted basis

3 - An ODCB:CPC ratio of less than 0.75:1 would adversely affect the rate of strength development; a ratio more than the formula quantity of 0.85:1 would lengthen the distillation cycle without significantly changing quality. A distributor should be used for best quality. The recovered ODCB is entirely satisfactory for reuse "as is."

4 - The use of agents other than stearic acid (Triton X-100, diglycol stearate, etc.) adversely affected rate of strength development. Less than the stipulated amount of stearic acid (3% of the pigment weight, on a water extracted basis) caused quality degradation; more offered no advantage.

5 - The use of a water spray nozzle in the still, plus the addition of tri cresyl phosphate (roughly 0.1% of the pigment, added initially and every 2 hours after the start of distillation) was found to satisfactorily control foaming during the ODCB steam distillation. Dow Corning "antifoam A" was considerably less effective than TCP. As additional insurance against pigment carry-over into the condenser, etc. with the risk of plugging the equipment, a demisting screen was installed in the vapor line leaving the still. This has functioned satisfactorily to date.

6 - Although volumes of approximately 60" (±1500 gal.) have been distilled without difficulty, 45" (±1200 gal.) is a more desirable starting volume.

7 - The still is best operated using the exit vapor pressure as a control. During the initial heat up, full steam can be used until a body temperature of 70°C (max.) is reached. At this temperature the large steam valves should be shut off, and the small jacket valve used (no sparger) thereafter. Using 15" of water as the maximum still pressure permissible, no foam-over should occur, and satisfactory still cycles should be attained.

8 - The distillation can be considered completed when the ODCB present in the distillate is 4% or less by volume (20cc/500cc or less). The still can be shut down when two consecutive samples (at least 15 minutes apart) indicate this end point has been reached.

F - Filtration and Packing

1 - Filtration of the still slurry has been no problem. Estimating the required press volume per pound

?
19 = 111222112121 2

2/day 1600 1/day
× 30
48000 24000

36000/mo av.

all [illegible] was refilled through [illegible] press.

36 chloroactions at 268 = 9648 thousands

13988# shipped [illegible]

9648 × 1.40 = 13988

13 days — 15000# = 800#/hr

of CPC (pack lot--dry basis) has been more difficult than for the crude. During the last campaign an average of 885# per batch was pressed in 22 frames in 241 press (+24#/ft.s), and the condition of the cakes was fair. The average filtrate conductivity, toward the end of the cycle, was as follows:

8	hours	-	1360 ohms
10	"	-	2200 "
12	"	-	2550 "
14	"	-	2770 "

Newark quality data indicate 2000 to 2500 ohms is a satisfactory end point.

2 - There were no problems associated with drumming this material.

G - Quality and Yield

The following data were taken from the March 1954 plant campaign of approximately 15,000 lbs.

1 - Average quality (versus SW-3457-1, the temporary standard)

Masstone - Light
Strength - 98:100
Tint - vvs blue, vs intense
5.3% Cu, 48.1% Cl, 94.4% extracted solids.

2 - Over-all yield was 1.765# packed green/# blue crude (100% basis). 36 chlorinations → 17,000 lbs.

H - Special Raw Materials

1 - Anhydrous aluminum chloride--from Ohio Apex.

2 - Ortho dichlor benzene--from Orchem.

3 - Stearic acid--triple pressed--from Merk & Co., or Neofat--18-53--from Armour & Co.

4 - Tri Cresyl Phosphate--179A (Celluflex)--from Celanese Corp.