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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

CONTINUOUS YE-698-D - MIXING AND VARIABLE STUDY

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: CONTINUOUS YE-698-D - MIXING AND VARIABLE STUDY

PERIOD COVERED: JUNE 1970 - DECEMBER 1970

SUBMITTED BY: J. F. HIGGINS JFH Date Submitted: 2/16/71

APPROVED BY: E. F. KLENKE, JR. EFK Date Released: 3/8/71

__ABSTRACT:__ Factors affecting the YE-698-D continuous process were studied in the laboratory continuous reactor, including mixing, acidity level, effect of split-strikes, continuous acidity level control, and the effect of residence times. Recommendations for plant control variables were made.

INTRODUCTION

YE-698-D has been prepared in the continuous unit about three times in the past few years. Although some reasonable quality products were obtained each time, the quality was not within standard limits. The runs were of too short a duration to evaluate variables and frequently periods of very poor quality were obtained. In view of the additional flexibility a working YE-698-D process would give the Newark Plant, it was decided to do further laboratory work to explore potential control variables and establish the principles upon which a workable process should be based.

Previous laboratory work had been done in a gravity-feed laboratory continuous reactor, and had been of limited duration. By using a pump-fed system, designed originally for continuous azo work, a more reliable system was designed.

Utilizing this system, which involved the first three tank analogs of 12 Building, the following areas were studied:

1. The effect of mixing per se on color.
2. The effect of acidity level on color.
3. The effect of split-strikes on color.
4. The utilization of continuous control of the acidity level.
5. The effect of residence time as a variable to control color quality.

EXPERIMENTAL DATA AND CONCLUSIONS

A. Mixing

The influence of agitation on the quality of the 2000#/hour concentration process for YE-698-D was investigated. Agitation was provided by variable speed Lightnin' mixers with a top speed of 320 rpm. A 60-30-10 split was employed. Tanks 1 and 3 were one-half gallon jars, while tank 2 was a 15 liter high battery jar. Speeds were varied in 100 rpm increments in each of the jars.

Expt.	Tank 1	Tank 2	Tank 3	Quality
1922-K-75	320	320	320 1930	Satisfactory
76	220	220	220	"
77	120	120	120	Flop
80A	120	320	320	Satisfactory
B	320	120	120	Sat.-dk. red vs. A-C
C	220	120	120	Sl red v. A
82A	320	220	220	wk. v. 80B
B	220	220	220	vs red v. 82A

Additional experiments at 320 rpm in all jars with reduced residence time in Tank 2 (from 12.5 mins. to 5.9 mins.) showed essentially no differences.

The following conclusions were drawn.

1. A minimum level of agitation is necessary in all tanks to obtain a product in the YE-698-D quality range. This is probably related to lead excess and nucleation since only the first tank appears critical (K-77, K-80-B, K-80-C).

2. Inadequate agitation in the first tank can be compensated for by increased agitation in Tanks 2 and 3. This probably facilitates subsequent solid solution formation.

3. When agitation is nominal in Tanks 2 and 3, the agitation speed in Tank 1 affects tint and hue markedly (K-80-B and K-80-C). Higher speeds gave a redder tint product probably by facilitating growth of larger particles.

4. Greater agitation in Tanks 2 and 3 contribute to weakness of $\pm$ 15% by indirectly facilitating crystal growth.

From a practical point of view, this may indicate that stronger redder products may be obtained in the plant by reducing jet speeds in Tanks 2 and 3, provided Tank 1 is already adequately agitated.

Generally the strength level is dependent on the acidity of the chrome and lead solutions.

B. <u>Acidity Level</u>

Study of the influence of agitation and acidity level on the color attributes of YE-698-D was covered. A 60-30-10 split was employed at two-agitation levels and three acidity levels. The acidity level is generated by adding a fixed quantity of nitric acid to the solution of sodium chromate/molybdate/sulfate while holding the lead nitrate pH constant. The agitation levels evaluated were 1) 320 rpm in all three tanks,

2) 320 rpm in the initial tank, and

3) 120 rpm in the second two tanks.

The data are as follows:

Expt.	Acidity Level	1st Tank pH	Mt - Str (vs YE-698-D) All at 320 rpm	Mt - Str (vs YE-698-D) 1st tank 320 rpm 2nd + 3rd 120 rpm
1922-K	(HNO_3)	-		
87	1 (max)	2.65 - 2.75	dk 15% weak	dk 10% weak
88	2 (2/3 max)	2.90 - 2.95	vs lt 3-5% str	s lt 10% str
89	3 (1/3 max)	3.15 - 3.25	lt 20% str	dull, muddy 20 str dk dull

The following conclusions were drawn.

1. A first tank pH range of 0.7 pH unit can cause a strength variation of ± 35%.

2. Acidity level substantially controls masstone depth and strength level, but mixing plays a roll.

3. Second and third tank agitation gives stronger products, with little masstone change except at the high strength level where the masstone and tint becomes dull and muddy.

Practically speaking this may indicate that, on a plant basis in the continuous unit, a nitric acid feed to control strength should be considered. Additionally it suggests again that variable speed jets in the second two tanks may be important in process control.

The demonstrated sensitivity of strength and masstone to acidity level suggests that improved OK straight on the batch level might be achieved by utilizing a concentrated chrome sufficient for several batches, and pipeline diluting during the strike itself.

C. Chrome Split

A study of the system was conducted to determine the optimum chrome split in YE-698-D.

The following conclusions have been drawn:

1. A 90-10 split appears to give the best quality with good strength and red tint (Exp. 97 + 98).

2. A 100% introduction in the first tank may work if the residence times are reduced, to avoid weakness.

Expt. 1922-K		Tank (Avg. Res. Time-Min.) (1 - 10.3 - 1) 1	2	3	Rubout	X-RAY
91-A	rpm	320	320	320	Str 10-15	Good pattern
	split	60	40	-		
91-B	rpm	320	120	120	Dull MT.str	More monoclinic
	split	60	40	-	v.yellow	
	(Electron micrographs also indicate more) (monoclinic in 91-B.)					
92-A	rpm	320	320	320	v.s.wk,	Some excess
	split	60	-	40	v.s.yellow	monoclinic
92-B	rpm	320	120	120	s lt MT, v.str.	Excess monoclinic and
	split	60	-	40	v. yellow	tetragonal solid soln.
93-A	rpm	320	320	320	Lt.str. yel.	High excess
	split	40	60	-		monoclinic
93-B	rpm	320	120	120	v.lt., v.st.	Excess mono + str.
	split	40	60	-	yellow (flop)	tetragonal ss (flop)
94-A	rpm	320	320	320	v. lt. str.	High mono and
	split	10	90	-	yellow	tetragonal (flop)
95	rpm	320	320	320	Lt. str.	Excess mono plus
	split	10	-	90		tetragonal
	(Electron micrographs show no change in particle size from (first tank to third tank. The particles are very small. (X-rays show no composition change. Here, all orange solid (solution formation and particle size growth took place in (the development (salt-HCl) step.					
96-A	rpm	320	320	320	Lt. str.	Slight monoclinic
	split	10	30	60	yellow	
	(X-rays show progressive orange solid solution formation (in each step. Electron micrographs show growth in each (step. Indications are final formation was in development (step.					
97-A	rpm	320	320	320	St $\pm$5% s lt MT	Excellent pattern
	split	90	10	-	red tint	
	(X-rays show almost complete orange formation by second (tank. Electron micrographs show substantial growth by (second tank.					
98-A	rpm	320	320	320	str. $\pm$5% dk MT	Excellent pattern
	split	90	-	10	red tint s redder	
99-A	rpm	320	320	320	Dk wk red	Excellent pattern
	split	100	-	-	(15%)	
100-A	rpm	320	320	320	Dk wk (15) red	Excellent pattern
		100	-	-	(s yel v. 99A)	
			(2.6)			

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X-ray and electron micrographs of in-process samples in experiments 91, 95, 96 and 97 give a good picture of the effect of split and particle size. Experiment 95 shows that almost all growth and transformation takes place during salt development whereas the reverse split in Experiment 98 shows the opposite with Experiment 96 showing the stepwise approach.

Based on the results obtained it was recommended to the Process Engineering group that a 90-10 split be tried in the next continuous YE-698-D run.

D. Controlled HNO_3 Feed

YE-698-D strength may be controlled by introducing HNO_3 in the first tank and omitting it from the chrome make using a 90-10 split. Study to optimize the conditions was demonstrated in Experiments 101-104.

The advantage of this is a much more responsive strength control, correctible when necessary. It might be applicable to YE-421-D and YE-637-D as well.

Expt. 1922-K		Tank (Avg. Res. Time-Min.) (1 - 10.3 - 1) 1	2	3	Rubout	X-Ray
101	rpm	320	320	320	Str (93) yell	Tr monoclinic
	split	90	-	10		
			(2.6m)		s dk MT	
	Adj pH 3.35 (first tank) separate HNO_3 addition					
102	rpm	320	320	320	yellow v.	Some mono
	split	100	-	-	YE-698-D + 101	tetragonal
					eq str	
	HNO_3 feed to pH 3.30 first tank.					
103	rpm	320	320	320	v. wk	tr. mono
	split	90	-	10	Dk MT	deep valley
				(10.6 min)		
	HNO_3 adj to 2.95 pH					
104	rpm	320	320	320	v. wk.	Sl excess mono
	split	90	-	10	DK MT	trace tetragonal
				(2.6)		
	HNO_3 to pH 2.80					

E. Residence Time

Optimum conditions for the controlled strike pH Moly Orange process were determined. With a 90-10 split, by varying residence times and pH in the first tank, "OK straight" quality has been obtained, as well as leads for variables. Optimum conditions are a strike pH of 3.30 with a short first tank residence time of about a minute; a ten minute second tank residence time and about two minutes in the third tank.

By shortening the second residence time strong yellow material can be obtained; longer time resulted in slightly weak redder products.

Expt.	Tank Avg. Res. Time-Min. 1 - 10 - 1	Rubout	X-Ray
1922-K			
105	rpm 320 320 320 split 90 - 10 (2.6m) HNO_3 pH 3.15	Dk MT v. Wk	Good pattern trace tetragonal
106	rpm 320 320 320 split 90 - 10 (2.6m) HNO_3 pH 3.30	Dk Str Yel	Good pattern
107	rpm 320 320 320 split 90 - 10 (0 min) HNO_3 pH 3.35	Lt Str Yellow	Some mono and tetragonal
108	rpm 320 320 320 split 90 - 10 (10.3 m) HNO_3 pH 3.3	s dk MT 90 s red	Good pattern
109	rpm 320 320 320 split 100 - - (10.3m) (2 m) HNO_3 pH 3.4	Dk wk	Good pattern tr. monoclinic
110	rpm 320 320 320 split 90 - 10 (13 m) HNO_3 pH 3.35	Dk MT 105 R^{20}	Good pattern