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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

FINAL REPORT

TITLE: HYPOCHLORITE TREATMENT OF POLYCHLOR CPC GREEN

PERIOD COVERED: MARCH, 1949 - MAY, 1949.

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DATE SUBMITTED: 8/15/49

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N42218

I - INTRODUCTION

The accumulation of a considerable inventory of sub-standard (blue and dull) polychlor CPC green pulp N-624, and of Green CPC toner, GT-674-D, at Newark, derived from the Newport plant, necessitated the investigation of some means for salvaging such stocks. Although the use of sodium hypochlorite for improving polychlor CPC Green quality had been explored previously at Newark without significant success, the urgency of the problem justified a re-investigation of the method with variations. The use of alkaline sodium hypochlorite for this purpose is not novel and is described in the industrial and patent literature (Ref. 1, 2). The work reported here represents an investigation of those conditions of hypochlorite treatment which produce the optimum tinctorial improvement in sub-standard polychlor CPC Green derived from the Newport plant, consistent with practical plant operations.

It is recognized that the extent of the response of a Green CPC to the hypochlorite treatment will vary with the nature of the impurities which give rise to the tinctorial deficiencies, and that the ultimate tinctorial properties of the color will depend on the inherent chemical and physical constitution of the pigment (i.e., chlorine content, particle size, etc.) plus the effect of those impurities that remain unaffected by the treatment. It may be reasonably assumed that the nature of the impurities present in a polychlor CPC Green will vary with the process employed for its synthesis and for the synthesis of the parent copper phthalocyanine from which it is derived.

II - SUMMARY

A plant process for the recovery of sub-standard polychlor CPC Green by treatment with alkaline sodium hypochlorite has been developed (Appendix I). The treatment consistently produces a considerable quality improvement (yellowness and intensity). The degree of improvement, however, varies from one sub-standard batch to another depending on the inherent quality of the material treated and the nature and quantity of impurities present. Pigment quality suitable for conversion into the various green CPC lakes and toners has been obtained in plant operations from previously unusable materials. A yield loss ranging approximately from 5-20% of starting pigment is experienced in the plant as a result of the treatment, the extent of loss being related somewhat to the initial quality of the sub-standard material.

III - EXPERIMENTAL AND DISCUSSION

The laboratory procedure for hypochlorite treatment of sub-standard polychlor CPC Green pulp (N-624) involves the addition of 25 gr. of "Clorox" (commercial 5.25% sodium hypochlorite solution) and 1.2 gr. of sodium carbonate to 25 gr. (dry basis) of Green CPC pulp in approximately 10% aqueous slurry, at 45-50°C for 4-6 hours, with agitation. Additional "Clorox" and sodium carbonate are added in the amounts specified above as necessary to maintain a hypochlorite excess for the total time of treatment, an excess being indicated by a positive starch-KI paper test. If a single addition of sodium hypochlorite persists for a period of two hours or longer, it may be reasonably assumed that the treatment is complete. At the completion of the treatment, the pH is adjusted to 1.0-2.0 with dilute sulfuric acid (1:1), and the pigment slurry filtered and washed free of sulfate and chloride. The presscake is then washed on the Buchner with a solution of 25% sodium carbonate.

washed free of alkali, and dried at 140°F.

The duration of the hypochlorite treatment and the quantity of hypochlorite required varies among the sub-standard batches. In the laboratory, from one to seven hours of treatment may be required and some lots may require eight times as much hypochlorite as do others. The products resulting from laboratory hypochlorite-treatment show good uniformity in quality and strength from lot to lot.

A variable study designed to determine the optimum temperature of hypochlorite treatment indicates 50°C. to be the best over-all temperature in comparison with 0°C., room temperature (27°C), 75°C, and 100°C. The lower temperatures require excessive treatment time, whereas the higher temperatures require excessive hypochlorite consumption. The 100°C run showed questionable effectiveness as regards quality improvement, presumably due to the instability of sodium hypochlorite at higher temperatures.

Final pH adjustment after the hypochlorite treatment is significant. A comprehensive series involving final pH adjustment at unit intervals (from 9 to 0.5) indicated that the lower pH values yield superior products and facilitate the rate of filtration of the treated pigment slurry.

Ammonia wash of the presscake is critical as regards pigment strength and tinctorial quality. If the product is not ammonia washed, or if the presscake is not washed free of ammonia-extracted impurities, a weak, dull product results.

Hypochlorite-treatment of crude polychlor CPC prior to solvent-grinding effects a considerably quality improvement over the untreated counterpart. The improvement, however, is not as great as that obtained by treatment of the solvent-ground counterpart. These differences are undoubtedly due to differences in the physical condition of the green at the time of treatment, the well-dispersed solvent-ground slurry responding more completely to treatment than does the poorly-dispersed crude.

IV - PLANT GREEN RECOVERY

The recovery campaign of accumulated stocks of sub-standard Newport green has been completed. A total of 9378 lbs. (dry basis) of sub-standard green CPC pulp (N-624) and 2593 lbs. of green CPC toner, GT-674-D, have been hypochlorite-treated. Products suitable for conversion to saleable green lakes and toners have been obtained.

REFERENCES:

1. ICI Departmental Ref. No. R.D.1046, 5/29/46, J.K.Thomson.
"Monastral Fast Green GS 20% Paste: Laboratory Development
of Sulphuric Acid Pasting Method and Preparation of Sealed
Sample RD/G/9222".
2. U.S.P. 2,276,175, "Phthalocyanine Pigment", M.H.Fleysher
and J. Ogilvie to Allied Chemical & Dye Corp.
3. Notebook 1278, experiments 51 to 84.

APPENDIX I

CODE: _____ N^o (B)GT-680-P Approved by:
 HST. 5167 SIZE: _____ EFE: 7-15-49
 DEAZO VAT: _____ HA: 7-15-49
 COUPLING VAT: _____ ET: 7-15-49
 STRIKE VAT: 208
 NON-BLEEDING JT: 7-18-49

NAME	NAME	INSTRUCTIONS	USE LBS.	N CODE	ACCT. LBS.
G.T.	1. Pour into strike vat:			624	600
	2. Adjust to 15" (900 G.)				
	3. Test and Record: pH _____, Normal 9.0+				
	4. Adjust to pH 10.0-10.5 _____ % If pH goes above 10.5, do not adjust downwards. Record: pH _____			7	±6
	5. Pour in 26 gallons		+280	660	+280
	6. Heat to 118-122°F				
	7. Stir 6 hours or longer at 118-122°F until tests indicate the hypochlorite treatment is complete. Maintain + KI test and pH 9.5-10.5 during this period.				
	NOTE: Test at 10 minute intervals, pH and KI test; record on reverse side of card. Whenever KI test is negative, add 13 gallons of N-660; and when pH falls below 9.5, add 3% 100% N-7. Rate of N-660 consumption will determine end point.			660	±1300
				7	± 25
	8. Adjust to pH 1.5-2.0 with N-27 diluted 1:1 _____ % If pH goes below 1.5 do not adjust upwards WATCH FOAM and CHLORINE GAS. Record: pH _____			27	± 50
	9. Press with agitation.				
	----- After washing the prescooke with water, wash it with dilute N-122 made up as follows:				
	10. Run 33" (2000 G.) water into strike vat.				
	11. Weigh and add		800	122	800

CODE: _____ EST. 516#

PROCESS: (B)32-680-2 DATE: 7-15-49

MAKING AREA NOTES

FE:HA:
JT:7-18-49

PRESSING AREA INSTRUCTIONS

Vat 208
Date
Time
Released by
Press No. 31
No. of Cakes 26
Press with Agitation
Wash to sulphate and chloride free.
Then wash with diluted ammonia
prepared in strike vat. Then wash
with water until conductivity of the
filtrate is equal to tap water.
Load in lined drums.
Samples For dry content.
Deliver to Control Laboratory
Drums to semi-finished warehouse.

(B) GT-330-F

STANDARD FORMULA NOTES

The previous code designation GT-330-F (A) represents polychlor GPO green paste (H-324) as received from the Newport plant. The present formula (B) GT-330-F is an expedient designed to improve the tinctorial quality of substandard lots of H-324. The treatment of substandard green GPO with sodium hypochlorite presumably destroys colored impurities which contribute to poor tinctorial quality (dull masstone and bluish).

The most suitable conditions for the hypochlorite treatment have been determined by variable studies with a view to optimum tinctorial improvement, minimum treatment time, and minimum sodium hypochlorite consumption. Inasmuch as sodium hypochlorite is unstable at high temperatures and at low pH values, temperatures in excess of those specified and pH values below those indicated may cause excessive destruction of sodium hypochlorite with little effect insofar as color improvement is concerned.

The duration of the treatment and the quantity of sodium hypochlorite required vary among the substandard batches. The initial additions of sodium hypochlorite are consumed quite rapidly (5-30 minutes). The later additions of hypochlorite persist for greater lengths of time (1-5 hours) and this rate of consumption gives some indication of the extent to which the treatment has progressed. Poorer lots of color will require greater quantities of sodium hypochlorite. There are some indications that when excessive quantities of sodium hypochlorite are used, subsequent additions of hypochlorite persist for much shorter periods of time than do the earlier additions. Arbitrarily, it can be stated that the treatment is completed when a six hour total time of treatment is up or when a single 15 gallon addition of hypochlorite persists for 2 hours or longer, assuming the specified temperature and pH additions have been maintained.

The final pH adjustment after hypochlorite treatment has been found to be significant. The lower pH values yield superior products and also facilitate the rate of filtration of the treated pigment slurry.

Ammonia wash of the presscake is critical as regards pigment strength and tinctorial properties. If the product is not ammonia washed, or if the presscake is not washed free of the ammonia-extracted impurities, a weak, dull product results.

The estimated yield from a 600 lb. batch of starting color is 516 lbs. based on an 86% average return for seven plant batches.

When the amount of H-324 is varied, the volumes and other ingredients are to be varied proportionately except the initial 23 gallons of H-330 which should remain the same as long as the H-324 amount is between 500 and 600 lbs.

An occasional batch of sodium hypochlorite solution (E-660) as received may be considerably alkaline so that the addition of H-7 during the treatment may be unnecessary. In such cases the pH will rise with each addition of sodium hypochlorite.

Substandard 61-374-2 dry green dye toner may be improved by the hypochlorite treatment, as described after first wetting the dry color in the Abbe-Lenart mixer. The plant 500 gallon Abbe-Lenart mixer can accommodate a 500 lb. batch charge. The color is added to an Aerosol OT solution prepared by dissolving 7.5 lbs. Aerosol OT in 15 gallons of water at the boil and diluting with 150 gallons of water in the mixer. The pigment slurry is mixed for two hours.

F. F. Ehrich
SIGNED: F. F. Ehrich 7-18-49

APPROVED: J. H. Cooper 7-18-49
H. Arnoul 7-21-49