Serial No. KN-51-4

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KN. 51-4

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

BASIC ZINC CHROMATE Y-563-D

DEVELOPMENT OF D, E, F, ECONOMY PROCESSES

SEPTEMBER 1950 - DECEMBER 1950

Charge: A-IC-8

SUBMITTED BY: J. O. MORRISON DATE SUBMITTED: Jan. 9, 1951

INTRODUCTION:

Imminent specification of mandatory use of "Insoluble Zinc Chromate" in several important military primer finishes prompted study directed toward correction of the excessive bulkiness of presscake and dry color, and consequent intolerable manufacturing costs, which had characterized the production of Basic Zinc Chromate Y-563-D by previous standard processes.

SUMMARY AND CONCLUSIONS:

Previous processes for manufacturing Y-563-D involved, essentially, chromic acid treatment of thoroughly dispersed zinc oxide slurries. The slurries demonstrated pronounced thickening throughout the successive bichromate and acid treatments, requiring use of relatively large volumes to prevent actual solidification in the strike vats. Very little, if any, reduction of bulk of the original slurry was effected in subsequent processing.

A modified process has been developed in which the zinc oxide predispersion step has been eliminated. Dry zinc oxide is now added directly to a solution of chromic acid (actually to a solution of bichromate, followed by acid treatment). This results in an initial predominately surface reaction between the chromic acid and relatively large aggregates of the zinc oxide. The final reaction product is sandy and compact, and demonstrates no tendency toward thickening (i.e. - increasing bulk) in slurry form except when deliberately subjected to prolonged intensive mechanical dispersion treatment. The product retains its desirable compactness through subsequent processing. Although obviously not entirely uniform, chemically, in slurry form, the final pulverized product has demonstrated satisfactory performance in the laboratory finish evaluations conducted to date.

One plant batch has been manufactured, to enable acceptance of a Navy Yard order for pigment. This order was filled with pigment of standard composition, and a portion of this batch has been submitted to Sales as a candidate for replacement standard (lot 21637).

Semi-works performance by the modified process has been completely satisfactory - processing characteristics being conducive to profitable manufacture if duplicated in the plant. In the case of the single plant batch the goal compactness of the semi-works pigment in presscake form was approached but not completely equalled. At the actual plant press-burden determined as optimum for this batch, the manufacturing cost demonstrates large reduction versus that of the previous process, but closer approach to the semi-works press burden goal is required in order to attain a better than marginal profit from the manufacture of the product. It is believed that the observed relative bulkiness of the first plant batch can be corrected by decreasing the extent or degree of zinc oxide dispersion through more rapid addition of the dry oxide or possibly by decrease in slurry volume or intensity of agitation.

A portion of the first batch was experimentally processed continuously in #12 Bldg. Borderline performance was obtained, definitely justifying further trial and mechanical study to correct the excessive accumulation of pigment in the centrifuge venturis. This program has been delayed because of the current capacity demand of other codes for production facilities.

The new standard (F) process formula and notes, describing the batch process actually used in the plant in manufacturing the proposed standard lot 21637, is an integral part of this report. Two earlier formulas, appended for reference, are:

(E) Plant scale up of semi-works performance, batch processing.

(D) Plant 12 bldg. scale up of semi-works strike, continuous processing.

DISCUSSION

The (F) formula notes, which follow, provide essentially complete information concerning the new process. The results of chemical analyses obtained subsequent to preparation of the notes provide the basis for the following additional conclusions (NB 1221-page 135):

1. There is no indication of significant variation or "drift" in composition among the three successively batch-processed portions of the strike. All are within government specification limits, and agree closely with each other.

2. The gravelly sediment from the floor of the vat is, as anticipated, relatively rich in ZnO. Although still within specification limits, this sediment differs appreciably in composition from the batch processed lots:

	ZnO	CrO_3
lot 21637	67.8%	18.7%
Vat sediment	70.8%	16.3%

As the result of the experimental processing sequence, no appreciable quantity of this sediment is present in the batch processed splits, essentially all of it having been transferred to 12 Bldg. with the result that it should be present in continuously processed lot 21639 only. In future production it will be desirable to sample packed production fairly closely to determine the effect of this sediment on composition uniformity, and whether the desirability of its segregation and, possibly, reprocessing, is indicated. Laboratory attempts to eliminate this sediment by a two-step process involving essentially initial preparation of potassium-free zinc yellow, followed by addition of zinc oxide to attain the standard composition, have not been promising. Elimination of sediment has been accompanied by excessive bulk (1221-63). Plant experimentation along this line will be desirable, however, in case the sediment is found to present a significant practical problem from the composition viewpoint.

3. The failure of the continuously processed portion (lot 21639) to meet specification limits of composition (because of low ZnO, high CrO_3 and excessive solubility) appears to be due at least in part to zinc yellow contamination, which is indicated by potassium analyses to be of the order of 2-1/2%. (1221, p. 135).

The preliminary laboratory study included trial of many surface active compounds as possible aqueous dispersants for the pigment slurries (1221 - 47, 48, 49). Some agents were slightly effective, the most notable being Blancol and Marasperse CB, but it appeared that at least 4% of agent on the pigment basis would be required to obtain slurries of the desired fluidity, and this approach to solution of the problem was terminated in favor of the economically more attractive approach ultimately embodied in the new process. Completely unpromising results were obtained in attempts to prepare the pigment by reaction of ZnO and CrO_3 in an Abbe' Lenart Mixer because of inability to obtain a fluid slurry at sufficiently high solids content to render the process economically attractive. Negative results were also obtained in an attempt to prepare a satisfactory product of specified ZnO to CrO_3 ratio (ignoring potassium) by dry blending zinc yellow with zinc oxide. The product demonstrated extremely poor film adhesion in primer finish evaluation.

REFERENCES

Experimental details are recorded in Research Notebook 1221, experiments 47 through 52, 54 through 61, and 63.

Development study records are also filed in Research Notebook 1221, under experiments 56, 58 and 60.

The chemical analyses of 1948 samples of competitive products manufactured by Imperial and by Mineral Pigments are recorded in Notebook 1221, page 125.

The following correspondence is pertinent:

Letter, "Basic Zinc Chromate", J. B. Callaway to R. H.Pohl, 9-22-50

TSR 4, "Phila. Naval Shipyard", J. A. Fredrickson, 10-12-50

Letter, "Y-563-D Economy Process Costs", J.O.M. to D.B.Killian, 10-20-50

Letter, "Basic Zinc Chromate," J.O.M. to R. H. Pohl, 11-6-50

Letter, "Y-563-D Sampling Lot 21637," J.O.M. to F.E. Bolton, 12-7-50

Letter, "Y-563-D Prospective Replacement Standard Lot 21637", J.O.M. to W.F.Spengeman 12-19-50

JOM:lg

(3330

CODE: Y-563-D K# (F)
GOAL: 17,584# SIZE:
DIAZO VAT:
COUPLING VAT:
STRIKE VAT: 260, 261, 262, 267
STD. HRS. NON-BLEEDING

APPROVED BY:
JOM: 11-8-50
HA: 11-8-50
BM: 11-13-50
JRG: 1-10-50

VAT	NAME: BASIC ZINC CHROMATE /C.G.6 INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS
PREP 1	1. OBTAIN, AND HOLD AT STRIKE VAT FOR STEP 8		525	
361 2	2. RUN INTO SCALE TANK 361 M_____ T_____ _____%		8	5089
S.V. 3	3. RUN 48" (4180G.) WATER INTO STRIKE VAT.			
	4. SET AGITATOR AT 16 RPM.			
	5. HEAT TO 74-76°F.			
	6. RUN SCALE TANK 361 INTO STRIKE VAT.			
	7. ADJUST STRIKE VAT TO 60" (5223G.) AT 74-76°F.			
	8. WEIGH AND DUMP IN IN 130-150 MINUTES OBTAINED IN STEP 1. RECORD: TIME STARTED _____. RECORD: TIME FINISHED _____.	12500	525	12500
	9. RUN IN IN 12-15 MINUTES FROM SCALE TANK 324 M_____ T_____ ± 31.64%	3938	28	1246
	10. STIR 5 MINUTES.			
	11. TEST AND RECORD: PH _____, NORMAL 5.5 - 6.0.			
	12. TEST AND RECORD: _____ °F., _____ ".			
	13. STIR 3 HOURS.			
	14. TEST AND RECORD: PH _____, NORMAL 6.0 - 6.5.			
	15. FLOOD TO 85" (7399 G.).			
	16. PRESS WITH AGITATION. AGITATOR MUST NOT BE STOPPED.			
	TIME START _____ TIME FIN _____ OPTR _____			
	" " " " " _____			
	" " " " " _____			

CODE: Y-563-D GOAL: 17,584#

PROCESS: (F) DATE: 11-7-50 HA

MAKING AREA NOTES JPL 1-10-51

EST. LOSS LBS.

REMARKS

PRESSING AREA INSTRUCTIONS

VAT

DATE

TIME

RELEASED BY

PRESS NO. 2

NO. OF CAKES 7 x 46

PRESS WITH AGITATION

WASH TO 5000 OHMS

MAKE FIRST TEST AFTER 4 HRS.

LOAD ON 35 CARS.

SPECIAL INSTRUCTIONS NON-BLEEDING.
SEE BACK OF CARD

SAMPLES

DELIVER TO

PRESSING AREA NOTES

DESCRIBE YOUR YIELD

RECOVERY CONDITIONS

EST. LOSS LBS.

CAKES USED

HOURS WASHED OHMS

DRYER CARS ACTUAL OR PULP CONTAINERS

NOTES ON SPECIAL INSTRUCTIONS

SAMPLED BY

RELEASED BY

DRYING AREA INSTRUCTIONS

TYPE	L.V.	H.V.	HURRICANE
HOURS	27	18	27
TEMP.	220°F.	220°F.	220°F.

MAKE FINGER FEEL TEST BEFORE PULLING

LUMP CONTAINER SEE CHART.

SPECIAL INSTRUCTIONS NON-BLEEDING.

SAMPLES

DELIVER TO

DRYING AREA NOTES

LUMP — OK — WET — SALTS — CONTAMINATED WITH

REMARKS

NO. DRYER CARS PULLED

LUMP WEIGHT

EST. LOSS LBS.

SAMPLED BY

RELEASED BY

GRINDING AREA INSTRUCTIONS

GRINDER NO. 10 HSP

SPECIAL INSTRUCTIONS NON-BLEEDING
PACK FROM DEAD TANK

SAMPLES 2 ENVELOPES AND 1 PINT CAN

DELIVER TO CONTROL LABORATORY.

DO NOT MIX BEFORE SAMPLING

PACKAGING SEE CHART.

GRINDING AREA NOTES

LUMP — OK — WET — SALTS — CONTAMINATED WITH

REMARKS

EST. LOSS LBS.

REMARKS

SAMPLED BY

DATE MIXED

QUALITY REMARKS

PRESSING AREA - SPECIAL INSTRUCTIONS

1. PRESS WITHOUT STRAINER
2. COLOR WILL PRESS IN 10-15 MIN. DO NOT OVERFILL.
3. BACKWASH TO VAT AFTER EACH PUMPING.
4. AGITATE CONTINUOUSLY EXCEPT WHILE MEASURING.
5. WASH WITH 130°F. WATER.
6. RECORD SPLITS BELOW:

SPLIT #	START INCHES	DIVIDE BY	USE INCHES	INCHES LEFT	OPTR.
1.	____"	7	____"	____"	____
2.	____"	6	____"	____"	____
3.	____"	5	____"	____"	____
4.	____"	4	____"	____"	____
5.	____"	3	____"	____"	____
6.	____"	2	____"	____"	____
7.	____"		ALL"	____"	____

Y-563-D (F)

STANDARD FORMULA NOTES

The "F" process represents initial plant modification of the "reverse strike reduced-bulking" experimental "E" formula.

"F" replaces "C" as standard formula, and differs from "C" as follows:

1. Batch size has been increased from 3200 lbs. to 17,584 lbs.

2. Press burden has been increased from 1067 lbs. to 2512 lbs. (per 78.7 cu. ft. pressload).

3. Dry zinc oxide is now slurried directly in dilute bichromate solution, in contrast to the "C" procedure in which bichromate liquor was struck into a separately prepared and thoroughly dispersed aqueous zinc oxide slurry.

GENERAL NOTES

The characteristic excessive bulkiness (both as presscake and as dry color) of pigment produced by the "C" process resulted in very unfavorable manufacturing costs which led to obsoletion of the product in 1949. Development of Basic Zinc Chromate pigmented Vinyl Resin finishes to positions of major importance as ship and aircraft primers has subsequently provided justification for study directed toward development of an economical manufacturing process.

The basic zinc chromate slurries produced by the new process are relatively coarse and granular. They are free from the gelling and solidification tendencies of the more finely dispersed slurries produced by previous prodesses. These physical changes have permitted increase of slurry pigment concentration from 0.93 to 2.2 lbs. per gallon, and increase of press burden from 13.5 to 31.9 lbs. per cu. ft. The latter approaches but does not equal the "E" process semi-works press burden of 56 lbs. per cu. ft. Attainment of the present 31.9 lb. plant press burden has provided a very considerable reduction in operating cost, but operative earnings at this press burden level are distinctly marginal and further development study is desirable, directed toward standardization on the basis of continuous processing (D formula) or batch processing at the semi-works presscake bulk (E formula), in order to attain a more satisfactory cost position.

Inasmuch as the mechanism of the cost reduction operation has involved a major change in type of slurry, a very finely divided slurry having been replaced by a very coarse gravelly slurry, it is quite probable that a concomitant decrease has been effected in completeness or uniformity of chemical reaction between the zinc oxide and the chromic acid (bichromate-muriatic acid). The chemical composition of the pulverized end product is normal, however, and to date no deficiency of the new products has been disclosed by laboratory primer evaluations.

STATUS OF PROCESS

Reverse-strike process development study to date has consisted of two semi-works strikes and one full size plant strike. All research development notes and records are recorded in Chemical Division Notebook 1221, Experiments 57, 58 and 60. In the case of the plant strike (made in 6 Bldg.), three pressloads were processed by batch procedure, permitting accurate determination of optimum press burden for that particular batch of slurry. The balance of the slurry was continuously processed through 12 Bldg. equipment. The batch - processing experience is considered adequate for preparation of the present "F" formula as a firm standard process. The continuous processing experience (lot 21639) was sufficiently favorable

to warrant additional study directed toward correction of the difficulties encountered - chiefly pigment accumulation in the centrifuge feed venturis. At present there is some uncertainty as to the reason for apparent abnormal composition of the continuously processed pigment. Analytical study is in progress to clarify this situation and the results thereof should provide a basis for measures designed to produce standard composition in future continuous process manufacture.

OPERATING NOTES

The reverse-strike D and E process slurries obtained in the laboratory, semi-works and plant have been free from any observed tendency toward thickening, gelling, or solidification. The sandy or gravelly character of the pigment produced by the new process introduces entirely different operating problems, arising from sedimentation of the slurry in vat outlets and transfer lines and hoses. The limited plant experience to date indicates that the sedimentation problem is not serious, provided the agitator is kept running continuously and provided the transfer lines are backwashed before and after each pumping. A uniform deposit of very coarse particle size pigment does, however, settle to the floor of the strike vat beneath the agitator blade and final "wash in" of this coarse sediment presents more than normal difficulty.

The most serious difficulties encountered to date in plant batch processing resulted from overloading the filter press. The character of the slurry is conducive to extremely rapid filtration. The pressing operation must be very carefully controlled to avoid overloading, with resultant excessive washing cycle and excessive difficulty in presscake removal and handling.

Contamination with zinc yellow must be prevented because of the importance of solubility and chemical composition discussed below.

The pulverized product packs readily in 50 lb. paper bags (N-566). It is desirable to avoid tumbling in the packing operation feed tank (i.e., "pack from dead tank") because the product balls quite readily when tumbled and, unless the tumbling operation were closely standardized, considerable variation in bulk density would probably occur.

QUALITY NOTES

Y-563-D is considerably less soluble than zinc yellow and also differs from the latter in chemical composition. Its ZnO/CrO_3 ratio is 4.5/1.0 and it contains no potassium, whereas the empirical formula for zinc yellow is $4\ ZnO.4CrO_3.\ 1\ K_2O.\ 3H_2O$. The respective solubility values (KCR-94) are 0.5% for Y-563-D (Navy Spec. maximum is 1.0%), and approx. 26% for Y-539-D. Y-563-D is an essential ingredient of newly developed vinyl resin metal protective finishes for both ferrous and non ferrous metals. Two important Navy Bureau of Ships specifications are: Metal Pretreatment (Wash Primer) Formula No. 117, and Primer No. 120. These two primer coats provide marked improvement in adhesion of finishes to underwater surfaces of ships. In these applications the most important pigment properties requiring control are believed to be chemical composition, freedom from electrolytes (chlorides), freedom from soluble lead, zinc, or other similar cations which cause gelation of the vinyl dispersion, and dispersion characteristics. Color is of significance only as an indication of general process control.

Pigment specification limits included in the Navy's Pretreatment (Wash Primers) Specification MIL-P-15328 are:

Constituent	Limits	Newark Analytical Method
Cr as CrO_3	16-19%	KCR-157
Zn as ZnO	67-72%	KCR-133
Water soluble salts	Max. 1%	KCR-94

Chloride and sulfate content are not limited, as such, by the Navy specification. In the absence of more definite information as to the effects of these constituents it is recommended that shipments be controlled, as in the past, below a maximum chloride level of 0.05% as determined by KCR-125.

The reverse strike products are essentially identical to the obsolete standard in chemical composition and have demonstrated satisfactory dispersion and stability performance in limited laboratory vinyl resin primer evaluations.

Available data indicate that the formulated 3 hour stirring period after acidification and before pressing is sufficient to permit attainment of reaction equilibrium but that a 90 minute period is insufficient. No drift in composition attributable to incomplete reaction was observed in the case of the three successive pressloads of the first strike, in which an age difference of 30 hours was involved between the initial and final filtration.

CONTROL VARIABLES

The composition of the product is controlled by the relative quantities of zinc oxide and of chromic acid (actually bichromate and muriatic acid) used. Decreasing the zinc oxide produces a less basic, more soluble product; increasing the zinc oxide is believed to result in the presence of free zinc oxide in the product. The effects of such variations on vinyl resin pigment dispersion properties are not known.

No other control variables have been developed for the new reverse strike process.

RECOMMENDATIONS

The following program is recommended for completion of standardization.

1. Establish reason for abnormal solubility and slightly excessive CrO_3 content of continuously processed stock (lot 21639). This may be due to:
   a. Contamination with zinc yellow (approx. 3 to 5%), or
   b. Inadequate draining of final centrifuge cake, or
   c. Inadequate washing of pigment, or possibly,
   d. Non uniformity of slurry in vat, with early removal of relatively zinc-rich pigment and late retention of relatively chrome-rich pigment.

2. Manufacture a full-size batch in 12 Bldg. strike unit, incorporating slight change in zinc-chrome ratio if need is indicated by results of (1) above. Apply all reasonable and proper physical processing variables to avoid pigment accumulation in venturis and to guard against (1a) and (1c) above.

3. Base choice between eventual batchwise and continuous type processing on results of one or more 12 Bldg. trials as in 2 above.

4. The difference in presscake bulk between the initial 6 Bldg. pigment (32 lbs./cu. ft.) and the semi-works pigment (56 lbs./cu. ft.) is probably the result of more complete, or finer, dispersion of the zinc oxide in the plant than was obtained in the semi-works. The only definitely known factor which would logically contribute to finer dispersion in the plant was considerably slower rate of addition of zinc oxide to the bichromate (195 minutes in the plant versus 60 minutes in the semi-works) with resultant considerable prolongation of the period during which a major portion of the zinc oxide - bichromate slurry was agitated prior to acidification and completion of reaction. In an attempt to approach the goal density (low bulk) of the semi-works product, which is of course desirable for continuous processing as well as batch processing, it would be desirable to assign sufficient manpower to the zinc oxide addition step to enable addition at a maximum rate, governed only by prevention of obvious lumping of the zinc oxide as it is added. No such lumping was observed in the 6 Bldg. strike, in which the addition rate was retarded both by non-availability of a helper and intermittent delivery of zinc oxide to the making area.

5. Other suggestions for possible reduction of bulking to the goal-cost semi-works performance level are:

Maintaining zinc oxide addition at maximum permissable rate,

a. Reduce agitator speed (applicable in 6 Bldg. only) to minimum gear setting (previous strike was made with medium speed),
b. Reduce initial bichromate volume substantially (say 40%). Observe batch closely and be ready to flood slurry if necessary to prevent stalling agitator. (This suggestion may possibly operate in the reverse sense to that which is desired).

6. Batch size has been arbitrarily fixed at a value slightly greater than that of zinc yellow. Lab. and semi-works results indicate that it may be possible to increase the size by from 20 to 60%; this is subject to confirmation in the plant.

7. St. Joe's Zinc Oxide, N-617, has been used exclusively in the semi-works and plant because of supply conditions. Trial of cheaper types of zinc oxide is recommended in the interest of economy.

STANDARD LOT

Pending completion of the standardization program, lot 21637, an optimum (standard) size batch-processed portion of the single plant strike to date, has been selected for use as temporary sampling material. Its composition is compared below with that of the obsoleted previous Y-563-D standard:

	New Lot 21637	Obsolete Lot 80166
Zn as ZnO	68.6%	67.8%
Cr as CrO_3	18.3%	18.4%
ZnO/CrO_3 Mol Ratio	4.62%	4.52%
Solubility	0.45%	0.85%
Cl	0.007%	0.020%
SO_3	0.061%	0.181%
K (flame photometry)	0.05%	-
Na " "	less than 0.025%	-

YIELD

Pending development of additional plant experience, and analysis of filtrates and wash water effluents for soluble zinc content, the original estimated goal yield for the "A" process has been retained. Scaled to the present batch size, (3200 x 12500 ZnO ÷ 2275 ZnO), this yield is 17,584 lbs.

For costing purposes, the 96.1% performance factor of the obsolete "C" process is recommended.

SUBMITTED BY: J.O. MORRISON 12/4/50

APPROVED BY : H. ARNOUL - 12/5/50

JOM:CC

(3334)

Cost Group - 6

CODE: _____ K# (D) Y-563-D
GOAL: 175844 SIZE: _____
DIAZO VAT: _____
COUPLING VAT: _____
STRIKE VAT: 12 Bldg. 21A, 21B, 22A.

APPROVED BY:
JOM: 10-16-50
HA: 10-18-50

JRG: 1-12-51

VAT	NAME: BASIC ZINC CHROMATE — INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS.
	1. Insert foot plug in strike vat outlet.			
	2. Run 45" (4320G.) water into strike vat.			
	3. Run in _____ M _____ %	_____	8	5089
	4. Adjust to 55" (5280G.) at 74-78°F.			
	5. Start Agitator.			
	6. Spot N-525 near chute area.			
	7. Weigh and dump in in 130-150 minutes	12500	525	12500
	Record: Time Started _____.			
	Record: Time Finished _____.			
	Record: Total Minutes _____.			
	8. Run in immediately in 12-15 M _____ + 31.64 %.	3938	28	1246
	Record: Time Started _____.			
	Record: Time Finished _____.			
	9. Stir 5 minutes.			
	10. Test and Record: pH _____, Normal 5.5-6.0.OPTR _____			
	11. Stir 3 Hours.			
	12. Test and Record: pH _____, Normal 6.0-6.5.OPTR _____			
	13. Test and Record: _____°F, _____".			
	14. Flood to 83" (7968G.).			
	15. Stir until finished centrifuging.			
	16. Remove foot plug from strike vat outlet.			
	17. Centrifuge with agitation at 16" / hour.			
	Record: Time Started _____			
	18. Counter current wash as follows:			
	A. Run 45 GPM dilution water at 80°F into centrifuge 67 wash port.			
	B. Run centrifuge 68 effluent into centrifuge 66 wash port.			
	C. Run 30 GPM of centrifuge 67 effluent to sewer and run remainder into centrifuge 66 head tank.			
	D. Run centrifuge 66 effluent to sewer.			
	19. Set fin drum indicator to _____, and pressure to _____#.			
	20. Adjust temperature of dryer section as follows:			
	1st. Section.			
	2nd. Section.			
	3rd. Section.			
	4th. Section.			
	21. Set dryer belt indicator to _____.			
	22. Set dryer discharge dampers to _____.			
	23. Run color to storage bin _____.			
	24. Grind HSP and pack.			
	TIME START _____ TIME FIN _____ OPTR _____			
	" " " " "			
	" " " " "			

CONTINUED ON PAGE 2.

VAT	PAGE: 2 CODE: (D)Y-563-D LBS: 17584 INSTRUCTIONS	USE LBS.	N-CODE	ACCT. LBS.

CENTRIFUGING RATE

CLOCK TIME	" IN VAT	ELAPSE TIME	" CENT	CLOCK TIME	" IN VAT	ELAPSE TIME	" CENT

K13731

(D) Y-563-D

FORMULA NOTES

12 BLDG. BATCH STRIKE - CONTINUOUS PROCESSING

The "D" process represents tentative plant formulation of a semi-works process developed to correct the characteristic excessive bulkiness of previous production (presscake as well as dry color) which resulted in unfavorable manufacturing costs, leading to obsoletion of the product in 1949. Justification for economy process study is provided by recent development of basic zinc chromate pigmented vinyl resin finishes to positions of major importance as primers for ships and aircraft. Both the "D" process and its companion "E" process (identical except for 6 Bldg. strike and batch processing) represent 40 X scale up of SW lot 1311, Research Notebook 1221-58.

The "D" process differs from the obsolete standard "C" process as follows:

1. Batch size has been increased from 3200 lbs. to 17,584 lbs.
2. 12 Bldg. batch strike and continuous processing have been substituted for the previously formulated 6 Building strike and batch processing.
3. The order of addition of zinc oxide and bichromate has been reversed. In the obsolete "C" process, bichromate liquor was struck into a separately prepared aqueous zinc oxide slurry. In the new process the dry zinc oxide is slurried directly in the (diluted) bichromate solution.

ECONOMY PRINCIPLE

The basic zinc chromate slurry produced by the new reverse process is relatively coarse and granular. It is free from the gelling and solidification tendencies of the more finely dispersed slurries produced by previous processes. These physical changes permit increase of slurry pigment concentration from 0.93 to 2.2 lbs. per gallon, and increase of press capacity from 1066 lbs. ("C" process) to 4400 lbs. (semi-works performance). Laboratory centrifuge tests indicate that, whereas slurry made by the old "C" process does not settle at all - remaining stable at full initial volume approximately 6 times the cake volume of zinc yellow, the new type slurries settle to approximately 1/3 their initial volume, or to double the normal cake volume of zinc yellow.

STATUS OF PROCESS

The "D" (12 Bldg. - Continuous Processing) and "E" (6 Bldg. - Batchwise Processing) formulas were written primarily for use in calculation of estimated manufacturing costs and were based on process development study consisting of 2 semi-works strikes. One 17,584 lb. plant batch has subsequently been struck in 6 Bldg. Approximately half of the slurry was continuously processed through 12 Bldg. equipment as lot 21639. As indicated in the following section, additional experience is necessary before final decision can be reached as to the practicability of continuous processing.

OPERATING NOTES

The reverse-strike D and E process slurries obtained in the laboratory, semi-works and plant have been free from any observed tendency toward thickening, gelling, or solidification. The sandy or gravelly character of the pigment produced by the new process introduces entirely different operating problems, arising from excessive sedimentation of the slurry in vat outlets and transfer lines and hoses.

The limited plant experience to date indicates that the sedimentation problem is not serious, provided the agitator is kept running continuously and provided the transfer lines are backwashed before and after each pumping. A uniform deposit of very coarse particle size pigment does, however, settle to the floor of the strike vat beneath the agitator blade and final "wash in" of this coarse sediment presents more than normal difficulty.

In the 12 Bldg. continuous processing trial, the most serious difficulty encountered was frequent accumulation of pigment in the centrifuge venturis. Additional study is necessary to correct this trouble. Processing conditions (instructions 17 through 22) remain to be established during the course of this study. Contamination with zinc yellow must be prevented because of the importance of solubility and chemical composition discussed below.

QUALITY NOTES

Y-563-D is considerably less soluble than zinc yellow and also differs from the latter in chemical composition. Its ZnO/CrO_3 ratio is +4.5/1.0 and it contains no potassium, whereas the empirical formula for zinc yellow is 4 ZnO.$4CrO_3$. 1 K_2O. $3H_2O$. The respective solubility values (KCR-94) are 0.5% for Y-563-D (Navy Spec. maximum is 1.0%), and approx. 26% for Y-539-D. Y-563-D is an essential ingredient of newly developed vinyl resin metal protective finishes for both ferrous and non ferrous metals. Two important Navy Bureau of Ships specifications are: Metal Pretreatment (Wash Primer) Formula No. 117, and Primer No. 120, These two primer coats provide marked improvement in adhesion of finishes to underwater surfaces of ships. In these applications the most important pigment properties requiring control are believed to be chemical composition, freedom from electrolytes (chlorides), freedom from soluble lead, zinc; or other similar cations which cause gelation of the vinyl dispersion, and dispersion characteristics. Color is of significance only as an indication of general process control.

Pigment specification limits included in the Navy's Pretreatment (Wash Primers) Specification MIL-P-15328 are:

Constituent	Limits	Newark Analytical Method
Cr as CrO_3	16-19%	KCR-157
Zn as ZnO	67-72%	KCR-157
Water soluble salts	Max. 1%	KCR-94

Chloride and sulfate content are not limited, as such, by the Navy specification. In the absence of more definite information as to the effects of these constituents it is recommended that shipments be controlled, as in the past, below a maximum chloride level of 0.05% as determined by KCR-125.

The reverse strike products are essentially identical to the obsolete standard in chemical composition and have demonstrated satisfactory dispersion and stability performance in limited laboratory vinyl resin primer evaluations.

Batch size has been arbitrarily fixed at a value slightly greater than that of zinc yellow. Lab. and semi-works results indicate that it may be possible to increase the size by from 20 to 60%; this is subject to confirmation in the plant.

St. Joe's Zinc Oxide, N-617, has been used exclusively in the semi-works and plant because of supply conditions. Trial of cheaper types of zinc oxide is recommended in the interest of economy.

Pending completion of the standardization program, lot 21637, a portion of batch-processed pigment from the single plant strike to date, has been selected for use as temporary sampling material. Its composition is included in the new Y-563-D (F) standard formula notes.

CONTROL VARIABLES

The composition of the product is controlled by the relative quantities of zinc oxide and of chromic acid (actually bichromate and muriatic acid) used. Decreasing the zinc oxide produces a less basic, more soluble product; increasing the zinc oxide is believed to result in the presence of free zinc oxide in the product. The effects of such variations on vinyl resin pigment dispersion properties are not known.

No other control variables have been developed for the new reverse strike process.

YIELD

Pending development of additional plant experience, and analysis of centrifuge effluents for soluble zinc content, the original estimated goal yield for the "A" process has been retained. Scaled to the present batch size,

(3200 x 12500 ZnO ÷ 2275 ZnO), this yield is 17,584 lbs.

For costing purposes, the 96.1% performance factor of the obsolete "C" process is recommended.

SUBMITTED BY: J. O. MORRISON-11/14/50

APPROVED BY : H. ARNOUL - 11/22/50

JOM:CC

Cost Group - 6

(3300)

CODE:_____ K# (E)Y-563-D

GOAL: 17,584# SIZE:_____

COUPLING VAT:_____

STRIKE VAT: 260-261-262-267

STD. HRS. 4.7 NON-BLEEDING

APPROVED BY:
JOM: 10-18-50
HA: 10-19-50

VAT	NAME: BASIC ZINC CHROMATE/G.G.6	USE LBS.	N. CODE	ACCT.LBS.
Prep. 1	1. Obtain, and hold at strike vat for Step 9.		525	
361 2	2. Run into scale tank 361 M_____ T_____ _____%	_____	8	5089
S.V. 3	3. Insert foot plug in strike vat outlet.			
	4. Run 48" (4180 G.) water into strike vat.			
	5. Agitator at 27 RPM.			
	6. Heat to 74-76°F.			
	7. Run scale tank 361 into strike vat.			
	8. Adjust strike vat to 60"(5223 G.) at 74-76°F.			
	9. Weigh and dump in 130-150 min. Obtained in Step 1. Record: Time Started_____ Record: Time Finished_____	12,500	525	12,500
	10. Run in 12-15 min. from scale tank 324 M_____ T_____ +31.64%	3,938	28	1,246
	11. Stir 5 minutes.			
	12. Test and record: pH_____, Normal 5.5-6.0			
	13. Test and record: _____F., _____.			
	14. Stir 3 hours.			
	15. Test and record: pH_____, Normal 6.0-6.5			
	16. Flood to 85" (7399 G.).			
	17. Press with agitation. Agitator Must Not Be Stopped. Press Operator to remove Foot Plug from Vat Outlet.			

Time Start_____ Time Fin._____ Optr._____

" " _____ " " _____ " _____

" " _____ " " _____ " _____

CODE: - GOAL: 17,584#

PROCESS: (E)Y-563-D DATE: JOM: HA 10-18-50

PRESSING AREA INSTRUCTIONS

Vat:

Date:

Time:

Released By:

Press No. 2 23

No. of Cakes: 4 x 46 4 x 46

Press with Agitation

Wash to: Chloride Free* at 110°F

Make first test after Hrs.

Load on 20 cars

Special Instruction: NON-BLEEDING

Must press with agitation.
Remove foot plug from vat outlet

*Use acidified silver nitrate solution.

Do not contaminate with zinc yellow.

DRYING AREA INSTRUCTIONS

Type:	L.V.	H.V.	Hurricane
Hours:	18	12	18
Temp.	220°F.	220°F.	220°F.

Lump Container: See chart.

Special Instructions: NON-BLEEDING.

Samples:
Deliver To:

GRINDING AREA INSTRUCTIONS

Grinder No. 10 H.S.P.

Special Instructions: NON-BLEEDING.

Do not contaminate with zinc yellow.
Avoid tumbling in mix tank - balls readily.

Samples: 2 envelopes and 1 pint can.

Deliver To: Control Laboratory.

Do Not Mix Before Sampling.

Packaging: See Chart.

(E) Y-563-D

FORMULA NOTES

#6 BLDG. STRIKE - BATCH PROCESSING

The "E" process represents tentative plant formulation of a semi-works process developed to correct the characteristic excessive bulkiness of previous production (presscake as well as dry color) which resulted in unfavorable manufacturing costs, leading to obsoletion of the product in 1949. Justification for economy process study is provided by recent development of basic zinc chromate pigmented vinyl resin finishes to positions of major importance as primers for ships and aircraft. Both the "E" process and its companion "D" process (identical except for 12 Bldg. batch strike and continuous processing) represent 40 X scale up of SW Lot 1311, Research Notebook 1221-58.

The "E" process differs from the obsolete standard "C" process as follows:

1. Batch size has been increased from 3200 lbs. to 17,584 lbs.

2. Press burden has been increased from 1067 lbs. to 4,400 lbs. per 78.7 cu. ft. pressload.

3. The order of addition of zinc oxide and bichromate has been reversed. In the obsolete "C" process, bichromate liquor was struck into a separately prepared aqueous zinc oxide slurry. In the new process the dry zinc oxide is slurried directly in the (diluted) bichromate solution.

ECONOMY PRINCIPLE

The basic zinc chromate slurry produced by the new reverse process is relatively coarse and granular. It is free from the gelling and solidification tendencies of the more finely dispersed slurries produced by previous processes. These physical changes permit increase of slurry pigment concentration from 0.93 to 2.2 lbs. per gallon, and increase of press capacity from 1067 lbs. ("C" process) to 4400 lbs. (semi-works performance). Laboratory centrifuge tests indicate that, whereas slurry made by the old "C" process does not settle at all - remaining stable at full initial volume approximately 6 times the cake volume of zinc yellow, the new type slurries settle to approximately 1/3 their initial volume, or to double the normal cake volume of zinc yellow.

STATUS OF PROCESS

The "D" (12 Bldg. - Continuous Processing) and "E" (6 Bldg. - Batchwise Processing) formulas were written primarily for use in calculation of estimated manufacturing costs and were based on process development study consisting of 2 semi-works strikes. One 17,584 lb. plant batch has subsequently been struck in 6 Bldg. Approximately half of the slurry was continuously processed through 12 Bldg. equipment. As indicated in the "F" formula notes, additional experience is necessary before final decision can be reached as to the practicability of continuous processing. Experience developed in connection with plant scale batch processing has been incorporated in the "F" formula, recently established as the standard process.

OPERATING NOTES

The reverse-strike D and E process slurries obtained in the laboratory, semi-works and plant have been free from any observed tendency toward thickening,

galling, or solidification. The sandy or gravelly character of the pigment produced by the new process introduces entirely different operating problems, arising from excessive sedimentation of the slurry in vat outlets and transfer lines and hoses. The limited plant experience to date indicates that the sedimentation problem is not serious, provided the agitator is kept running continuously and provided the transfer lines are backwashed before and after each pumping. It was found unnecessary in the plant to use the formulated foot-plug technique which had been essential in the semi-works. A uniform deposit of very coarse particle size pigment does, however, settle to the floor of the strike vat beneath the agitator blade and final "wash in" of this coarse sediment presents more than normal difficulty.

In the plant batch-processing trials, the most serious difficulties encountered resulted from overloading the wash press, viz.: excessive washing cycles and excessive difficulty in removing the presscake from the press and in loading drier pans. The character of the slurry is conducive to extremely rapid filtration as well as to excessive cake packing. Pressing must be carefully controlled to avoid overloading.

Contamination with zinc yellow must be prevented because of the importance of solubility and chemical composition discussed below.

QUALITY NOTES

Y-563-D is considerably less soluble than zinc yellow and also differs from the latter in chemical composition. Its ZnO/CrO_3 ratio is +4.5/1.0 and it contains no potassium, whereas the empirical formula for zinc yellow is 4 ZnO.4CrO_3. 1 K_2O. 3H_2O. The respective solubility values (KCR-94) are 0.5% for Y-563-D (Navy Spec. maximum is 1.0%), and approx. 26% for Y-539-D. Y-563-D is an essential ingredient of newly developed vinyl resin metal protective finishes for both ferrous and non ferrous metals. Two important Navy Bureau of Ships specifications are: Metal Pretreatment (Wash Primer) Formula No. 117, and Primer No. 120. These two primer coats provide marked improvement in adhesion of finishes to underwater surfaces of ships. In these applications the most important pigment properties requiring control are believed to be chemical composition, freedom from electrolytes (chlorides), freedom from soluble lead, zinc, or other similar cations which cause gelation of the vinyl dispersion, and dispersion characteristics. Color is of significance only as an indication of general process control.

Pigment specification limits included in the Navy's Pretreatment (Wash Primers) Specification MIL-P-15328 are:

Constituent	Limits	Newark Analytical Method
Cr as CrO_3	16-19%	KCR-157
Zn as ZnO	67-72%	KCR-133
Water soluble salts	Max. 1%	KCR-94

Chloride and sulfate content are not limited, as such, by the Navy specification. In the absence of more definite information as to the effects of these constituents it is recommended that shipments be controlled, as in the past, below a maximum chloride level of 0.05% as determined by KCR-125.

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For costing purposes, the 96.1% performance factor of the obsolete "C" process is recommended.

SUBMITTED BY: J. O. MORRISON - 12/4/50

APPROVED BY: H. ARNOUL - 12/5/50

JOM:CC