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CONFIDENTIAL

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Progress Report

POLYMER K - PIGMENT N - $N_{10}.H_2O$

SEMI-WORKS AND PLANT DEVELOPMENT
AA-2-P AND AA-3-5

Period Covered DECEMBER 8, 1949 - DECEMBER 31, 1950

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

POLYMER K - PIGMENT N - $NiO.H_2O$

SEMI-WORKS AND PLANT DEVELOPMENT AA-2-P AND AA-3-P

DECEMBER 8, 1949 - DECEMBER 31, 1950

Charge: A-IIC-258

SUBMITTED BY: J. O. MORRISON DATE SUBMITTED: 1-4-51

APPROVED BY: B. H. PERKINS DATE ISSUED: 1-15-51

CONTENTS

INTRODUCTION:

This report summarizes study conducted at the request of the Finishes Division of F. and F., directed toward the development of plant processes for manufacturing Hydrous Nickel (II) Oxide and flushing it in alkyd resin. The product was designated as "Pigment N" throughout the study. It has subsequently been designated as "Polymer K" by F. and F.

In an extension of earlier work on the fortification of lacquer and alkyd films by hydrous iron oxide, F. and F. found Pigment N (hydrous nickel (II) oxide) to be the most effective and generally desirable of the several oxides studied, not only from the viewpoint of film fortification alone, but also because the extreme transparency and optical clarity of Pigment N permits attainment of novel tinctorial effects hitherto unapproachable in finishes of acceptable durability.

SUMMARY AND CONCLUSIONS:

The Pigments Department Chemical Division was requested to develop practical plant processes for the manufacture and alkyd flushing of Pigment N, based on laboratory formulas supplied by F.and F. The development program has culminated temporarily with initial plant manufacture and determination of manufacturing costs. The plant product was equal in clarity and durability to semi-works products, which were, in turn, reportedly superior to the laboratory products which had aroused F. and F.'s original interest in the development.

Process standardization remains to be completed and is contingent upon authorization of further production. Guidance for the future program has been provided in the standard manufacturing formulas and notes included in this report. Previously specified modifications in existing plant flushing facilities are prerequisite to routine manufacture of flushed products.

PATENT SITUATION:

Patent aspects of the development and application of Pigment N are under the jurisdiction of F. and F. None of the operations involved in Newark processing appear patentable per se.

GENERAL DISCUSSION

Note:- This section supplements the standard formula notes which are included in this report, and which contain all major conclusions derivable from the development study.

LABORATORY FORMULAS

The formula originally recommended in F. and F.'s Philadelphia Laboratory Memo Report M-273 (Nov. 15, 1949) specified reaction of nickel sulfate with sodium hydroxide, washing by repeated filtration

and decantation, and flushing into RC-448 alkyd at P/B = 1/2. The report indicated that the major portion of their work had involved precipitation of the hydrous oxide from nickel chloride rather than from the sulfate, but that they had encountered serious difficulties in washing the precipitate sufficiently chloride free to avoid blistering on exposure and were recommending the use of nickel sulfate because they considered sulfate ions to be less destructive in paint films than chloride ions. (Informal advice from F. & F. personnel indicates that the latter viewpoint has been reversed by the results of recent independent study involving systems in which corrosion is not a controlling factor.)

In a supplemental report dated Dec. 14, 1949, Philadelphia Laboratory retracted the sulfate recommendation because of inferior optical clarity and specified the use of nickel chloride for optimum clarity, as well as a maximum limit of 0.2% Cl on the pigment solids basis for satisfactory blistering resistance. Their proposed washing cycle involved four decantations, filtering and reslurrying, followed by two decantations and ultimate filtration. As related below, it was later established during the Newark development study that adequate salt removal for standard blister-resistance can be obtained by a one-cycle wash-press operation, and that the actual tolerable Cl content is somewhat greater than ten times the limit specified above, the major portion of the discrepancy in specification limits being due to inadequacy (incomplete extraction) of the analytical method on which the initial specification was based.

A final laboratory formula revision, transmitted informally by F. and F. on Jan. 11, 1950 (Newark N.B. 1361-17), substituted RC-5078 resin solution for 75% of the initially specified RC-448. This change, initially made in the interest of increasing ultimate film hardness, appeared to increase considerably the quantity of breakout water (and contained salt) during flushing, and also appears independently to have contributed importantly to the excellent optical clarity of semi-works and plant flushed products.

NEWARK LABORATORY STUDY

Preliminary laboratory series were run, using nickel sulfate as initially specified, to develop familiarity with the precipitation process and to investigate possible variables for accelerating salt removal either by decantation or by press-washing. The limited quantity of products obtained precluded flushing by orthodox vacuum mixer procedures. Attempts to apply micro-flushing techniques were partially successful but the recognized uncertainty as to significance of results obtained from such tests prompted the decision to conduct the major portion of the development study at semi-works batch size. One promising result indicated the possibility of accelerating filtration by heat treatment of the slurry, but attempts to confirm this in the semi-works were unsuccessful.

DEVELOPMENT OF STANDARD PROCESSES

A pilot semi-works batch (lot 1143 and splits) was struck from nickel chloride following receipt of revised specifications from Philadelphia Laboratory, and experimentally processed with the following results:

(a) The pressing and press-washing characteristics of the slurry were similar to those of iron blues (perhaps intermediate between B-300-D and B-63-D), and definitely better than those of our more difficultly processed products such as Pigment Green B.

(b) Excessive press-washing did not attain the 0.2% maximum Cl limit specified by F. and F. Actual analysis of the washed pigment indicated Cl content to be 2.3%.

(c) Heat treatment of a portion of the slurry produced no improvement in processing characteristics.

(d) Decantation washing, attempted on a portion of the slurry, appeared to be completely impractical.

(e) Attempts to further decrease the salt content of the washed presscake (2.3% Cl as is) by reslurrying resulted in peptisation which precluded the possibility of subsequent filtration or decantation.

Laboratory flushing of the press washed (2.3% Cl) pulp, at Philadelphia, produced mill base of excellent initial quality and it was agreed to proceed promptly with the manufacture of three additional semi-works batches, each to be flushed at Newark, with demonstration of mutually satisfactory reproducibility and satisfactory blistering resistance by accelerated test to serve as sufficient basis for manufacture of a 600 lb. plant batch.

Two additional semi-works batches (1160 and 1164) were made promptly and duplicate 2.5 gallon flushed mill bases of each prepared at Newark using the modified resin composition later incorporated in the standard AA-3-F formula:

Pigment/RC-448/RC-3078 = 1.0/0.5/1.5

The pigment processing characteristics as well as the chloride contents of the new batches checked those of lot 1143. During the course of analytical work at Newark it was demonstrated that the analytical procedure previously employed at Philadelphia resulted in extraction of only approximately 10% of the total chloride actually present in the semi-works products. The semi-works flushed products possessed excellent resistance to blistering in accelerated tests, and were sufficiently promising in general quality to justify authorization of plant manufacture prior to completion of the full three-batch program.

One 600 lb. plant batch of pigment was struck March 27, 1950. A semi-works processed portion of the plant slurry was normal in processing characteristics, but abnormal washing was experienced in the plant, with unexpectedly early appearance of peptization bleed which compelled termination of washing. The Cl content of the plant pulp, however, was normal at 2.2% on the solids. Upon opening the filter press it was obvious that the press burden was considerably below optimum, the "cake" being abnormally quite fluid. Corrective measures have been incorporated in the standard AA-2-P formula.

Two plant batches of flushed base were manufactured. The processing of each batch was grossly complicated by unsuitability of heating facilities for the distillation cycle and various other difficulties of relatively less serious character, all of which have been discussed in the writer's letter of 9-11-50 to J. H. Bailey, "Flushing Facilities - Building #12." Further complications resulted, in the case of the first batch, from the abnormal fluidity of the plant presscake. These were corrected in a single semi-works flushing by modification in mixer loading technique. The correction was satisfactorily confirmed in the second plant flushing, and the modified technique has been incorporated in the standard AA-3-F process and discussed in the formula notes. Despite the operational difficulties encountered, each of the flushed plant batches was fundamentally satisfactory in initial properties and in durability.

No final decision as to future manufacturing policy has been made to date. In the event that manufacture is resumed at Newark it will be necessary to effect recommended modifications in plant flushing facilities and complete the plant standardization study along the lines suggested in the AA-2-P and AA-3-F formula notes.

PIGMENT VARIABLE STUDIES

Heating the slurry prior to filtration (lots 1144, 1169) has no beneficial effect on processing characteristics or yield, and apparently is detrimental to quality in that flushed bases of such pigments are abnormally seedy (1351-27-28).

As discussed under "Yields" an indication was obtained in the case of lot 1319 that significant improvement in yield may result from use of very mild agitation conditions during strike. This batch, however, was made for experimental use in Duco subsequent to termination of active study at Newark, and therefore was never evaluated in standard AA-3-F. The lead merits further investigation.

An attempt was made to establish the maximum Cl tolerance limit of Pigment N. The available results (1351-52) indicate that extremely superficial washing - to approx. 150 ohms (6.6% Cl on presscake solids, 2.3% Cl in resulting base after 65% water decant) - is adequate insofar as Philadelphia's practical Delaware exposure

blistering results are concerned. A more cautious interpretation, however, suggests tentative specification of a wash water effluent specific resistance end point in the 1000-1500 ohms range, with 3 to 4% Cl on the pressoake solids, or 1 to 2% Cl on the flushed mill base pigment after breakout. Actually, indications have been observed that the maximum Cl tolerance may be fixed on the basis of optical clarity of the mill base rather than on the basis of blister susceptibility. The foregoing considerations confirm the writer's previous view, expressed in the AA-2-P formula notes, that incipient peptization bleeding in the wash press effluent is an indication of adequate chloride removal.

One semi-works batch (1168) was struck from nickel sulfate rather than nickel chloride, using the standard stoichiometric quantity of caustic, and was washed to 4% SO_4 on the solids. The mill bases prepared therefrom (1351-23-25) amply confirmed Philadelphia's prediction of substandard turbidity or milkiness. Based on an apparent laboratory lead, a second sulfate batch was made in the semi-works (1191) using twice the stoichiometric quantity of caustic. Sulfate analyses of the pulp (1.8%) and the base (2% after 67% breakout) are in conflict, unresolved to date. The resulting flushed mill base (1351-49) was satisfactory in clarity although inferior to normal chloride bases in dispersion characteristics. No attempt has been made to correct the dispersion characteristics, because accelerated blistering tests at Philadelphia indicated the sulfate mill base to be extremely poor. Subsequent Delaware exposure evaluation, however, has not confirmed the accelerated test, but indicates the sulfate product to be satisfactorily blister resistant on practical exposure. This reopens the desirability of further study to correct the dispersion deficiency and confirm the blister resistance in order to realize the significant potential ingredient economy which would result from the use of the sulfate pigment process despite the increase in caustic. Specific surface determinations failed to differentiate significantly between the two sulfate pigments, or between sulfate and chloride pigments.

FLUSHING VARIABLE STUDIES

The AA-3-F formula notes discuss the currently available known facts and plausible hypotheses concerning optimum flushing conditions, except for an attempt to establish a maximum tolerable HgO limit in the flushed base (1377-42). The results of this attempt indicate that satisfactory optical clarity and transparency as observed through the mixer sight-glasses provide sufficient evidence of adequate water removal (to 2-1/2% or less, by toluene distillation). Inasmuch as samples of base withdrawn while still opaque and milky (at 3.2% or greater H_2O content) gelled very rapidly it is desirable to review Philadelphia's complete evaluation of the 1377-42 mill bases prior to resumption of manufacture.

A standard 2.5 gallon mixer process for flushing normal A-2-P is given in 1351-56, and a process for flushing abnormally fluid A-2-P is recorded in 1351-57. Experience with the 2.5 gallon

mixer has been much more satisfactory than that with the 0.75 gallon mixer, possibly because of less frequent use of the latter and unfamiliarity of personnel with its distillation characteristics. A very high incidence of substandard dispersion properties resulted from attempts to use the smaller mixer.

At the request of Philadelphia Laboratory, normal pulp was flushed into RC-448 alone (1351-44) according to the formula originally proposed. The product was extremely turbid (milky) compared to a control (1351-45) flushed in standard formula. This effect was duplicated with another lot of pigment in experiments 1351-42 and 46.

Also at Philadelphia Laboratory's special request, a flushed base (1377-45) was prepared in which RC-3075 was substituted for RC-3078. The product appeared inferior to normal products in color, dispersion and turbidity.

TESTING

The flushed product must be completely free of turbidity or milkiness when reduced to enamel composition, applied as a 3 mil clearance film over black, and baked. This property has been designated "optical clarity" in this report. It is not to be confused with "opacity", at least in certain restricted or specialized applications of the latter term. For example, an "opacitometer" designed for controlled-view comparison of uniform films of alumina hydrate inks with numerically graduated standard white films of increasing opacity was found to be completely useless in distinguishing between Pigment N enamels of widely different milkiness.

A prescribed method for conducting the enamel test is given in the AA-3-P formula notes. As also stated in the notes, however, the clarity of the mill base can always be accurately appraised by looking at a sample of the mill base in a glass jar or on a bright spatula.

The only certain test of AA-2-P presscake quality available at present is a vacuum-mixer flushing by the AA-3-P process. Attempts to develop micro flushing rubout type tests have been completely unsuccessful, but it is suggested that a test involving change can mixing of presscake and resin solution followed by evaporation transfer using the back rolls, only, of a warm (120 - 140°F) roller mill be investigated, when study is resumed.

PHYSICAL INSTABILITY OR DRIFT

Pigment N demonstrates the generically characteristic tendency of hydrous oxides to undergo growth of particle size during aging of aqueous presscake, with consequent loss of transparency which eventually results in inability to produce satisfactory optical clarity of flushed mill bases. The rate of this "drift" has been tentatively established, as discussed in the AA-2-P formula notes,

to be sufficiently moderate to forebode no difficulty in routine manufacture of flushed Dulux bases provided the two week age limit specified in the AA-2-P and the AA-3-F formula is respected. No information is available as to age specifications for preparation of Duco bases; all investigation of the latter has been the exclusive responsibility of F. and F.

Insofar as the optical and rheological stability of flushed bases is concerned, Philadelphia Laboratory stated at the beginning of the development study that no problem had been encountered up to that time. None has been reported subsequently.

PHYSICAL STUDIES

Specific surface measurements of dried pulp samples, as well as the relative lack of definition of X-ray diffraction patterns of aqueous presscakes, indicate the ultimate crystallite size of Pigment N to be in a range having .01μ as its maximum (RLM report 50-29). Electron micrographs of flushed mill bases also support this conclusion, since all objects larger than the practical limit of resolution (.01μ) have the appearance of aggregates rather than of crystallites.

In experimental application, of very limited extent, none of these techniques distinguished between samples of satisfactory pigment or mill base and samples having unsatisfactory optical clarity. No further attempts were made to develop fundamental data relating optical properties to crystallite size, because of the lack of readily available methods for precise size measurement in the region of interest. X-ray scattering has been recommended by Dr. Hanks of the Newark Physics Group as the method most likely to be capable of development to a satisfactory applicable state if need for such data arises.

Direct evidence of crystallite growth during aging of aqueous presscake was provided by a significant reduction in the quantity of resin required to effect transfer in the flushing process. Available data, with estimated precision of $\pm$ 5% or better, indicate that plant pigment had decreased in particle size by 38% after 5 months aging as presscake, and that a semi-works pigment had decreased by 56% after 7 months aging (1377-38, 39).

CHEMICAL COMPOSITION

Pigment N is essentially $NiO.H_2O$. Basic nickel salt, if present at all, comprises less than 0.5% of the weight of satisfactory pigment precipitated from chloride, and approximately 1% of the weight of unsatisfactorily milky pigment precipitated from sulfate by the stoichiometric caustic process. (General Laboratory Analytical Report AA-2-P dated 4-12-50). The empirical formula of standard quality semi-works pigment (1160) after toluene distillation followed by drying at 160°C is 1.00 NiO. 1.02 H_2O. Average Cl analyses correspond to approximately 3 to 4% NaCl. Analysis of the plant lot checks that of the semi-works products very closely.

Cost Group - 15

CODE: K#(A) A-2-P Approved by:
GOAL: 80%# SIZE: JOM: 3-7-50
EST. FROM. YLD. 516# EWA: 3-7-50
COUPLING VAT: GWO: 3-7-50
STRIKE VAT: 209

(3136) Std. Hours ____. NON-BLEEDING

Vat	NAME: PIGMENT IN PULP	USE LBS.	N. CODE	ACCT. LBS.
209 1	1. Run 15" (6000.) water into vat 209.			
	2. Start Agitator.			
	3. Weigh and dump in	1470	610	1470
	4. Stir 10 minutes or longer to dissolve.			
330 2	5. Run 56" (6270.) water into vat 330.			
	6. Start agitator.			
	7. Weigh and pour in K____%		7	515
	8. Adjust to 56" (9800.) at 79-81°F.			
209 3	9. When N-610 is completely dissolved, adjust vat 209 to 25" (10000.) at 79-81°F.			
	10. Test and record: pH____, normal 3.9-4.2.			
	11. Strike vat 330 without agitation at 79-80°F. into vat 209 at 79-81°F. on the surface in 29-32 minutes. Record: Time started: ____° Record: Total minutes ____°			
	12. Stir 5 minutes.			
	13. Test and record: pH____, Normal 10.6-11.0.			
	14. Press without agitation.			

Time Start____ Time Fin____ Optr____

" " ____ " " ____ " ____

CODE: _____ EST. 516#

PROCESS: (A) A-2-P DATE JON: 3-7-50

PRESSING AREA INSTRUCTIONS

Vat : _____

Date: _____

Time: _____

Released By: _____

Press No. : 20

No. of Cakes: 46

Press without agitation

Wash To 2,400 Ohms

Make first test after 24 hrs.

Load in 4 drums - use plastic liners

Special Instructions: Non-Bleeding.

Soda ash wash all equipment
Wash with warm water (110° - 120°F)

Samples: _____

Deliver To: _____

APPROVED BY:

CODE: K#(A)A-3-P JOM 4-12-50

Cost Group - 14

GOAL: 2194# SIZE

EST.PRODN.YLD. 1969#

COUPLING VAT:

STRIKE VAT:

(5299) NON-BLEEDING

VAT	NAME: FLUSHED PIGMENT N	USE LBS.	N. CODE	ACCT.LBS.
BAKER PERKINS MIXER	1. Install recorder chart in temperature controller.			
	2. Set temperature controller at 10°C.			
	3. Weigh and shovel into mixer.	———	A-2-P	150
	4. Start mixer with top raised.			
	5. Run in from scale drum through 2" line in 15 minutes	208	693	208
	6. Run in N-694 from scale drum through 2" line no faster than 4 lbs. per minute. Watch mixer constantly. Stop N-694 when water is about to break out. Record N-694. Continue mixing until water separates.	———	694	———
	7. Decant repeatedly until all separated water has been removed from mixer.			
	8. Weigh and shovel into mixer	———	A-2-P	30
	9. Start mixer.			
	A. When water sheds, decant repeatedly until all separated water has been removed, or			
	B. If charge in mixer becomes crumbly and does not shed water within 15 minutes, slowly add N-694 as in Step 6 until breakout occurs.	———	694	———
	C. If charge in mixer remains pasty and does not shed water within 5 minutes, check here ( ) stop mixer, and proceed with Step 10.			
	10. Weigh and shovel into mixer	———	A-2-P	30
	11. Repeat Step 9. Check A or B or C below:			
	A. ( ) water shed and completely decanted.			
	B. ( ) crumbly after 15 min. Added N-694 to shed	———	694	———
	C. ( ) pasty after 5 min. No shedding.			
	12. Weigh and shovel into mixer	———	A-2-P	30
	13. Repeat Step 9. Check A or B or C:			
	A. ( ) water shed and completely decanted.			
	B. ( ) crumbly after 15 min. Added N-694 to shed	———	694	———
	C. ( ) pasty after 5 min. No shedding.			

(COMB'D ON PAGE 2.)

VAT	PAGE: 2 CODE: A-3-F LBS:	USE LBS.	N. CODE	ACCT.LBS.
	14. Weigh and shovel into mixer.	———	A-2-P	30
	15. Repeat Step 9. Check A or B or C: A. ( ) water shed and completely decanted. B. ( ) crumbly after 15 min. Added N-694 to shed	———	694	———
	C. ( ) pasty after 5 min. No shedding.			
	16. Weigh and shovel into mixer	———	A-2-P	30
	17. Repeat Step 9. Check A or B or C: A. ( ) water shed and completely decanted. B. ( ) crumbly after 15 min. Added N-694 to shed	———	694	———
	C. ( ) pasty after 5 min. No shedding.			
	18. Close mixer.			
	19. Calculate total N-694 added in steps 6 thru 17. Record total ____ lbs. Subtract total from 900 lbs. Very slowly add the required difference through the 2" line in 2-3 hours. Inspect charge closely and frequently. If lumps appear, stop N-694 at once until charge is again uniform, then resume N-694 addition. Record time started and time finished, on temperature recorder chart.	900	694	900
	20. Very slowly add through the 2" line in 1 hour. Keep batch lump-free and uniform as in step 19.	362	692	362
	Note: If necessary, the operation may be shut down, at this point only, for 16 hours or less. If shutdown is desired: A. Stop mixer and scrape down sides. B. Run in through the 2" line a one-half inch layer of N-690 onto the surface of the charge. C. Lock out drive motor until ready to proceed.	———	690	———
	21. Open mixer and start mixing.			
	22. Weigh and pour in during 5 minutes	11	695	11
	23. Drain distillate exhaust lines behind mixer.			
	24. Open condenser spray valve 1-8 turn.			
	25. Close mixer and distillate drain valves.			
	26. Start vacuum.			
	27. Set temperature controller at 50°C.			
	28. Continue mixing under vacuum at 50°C. until charge becomes dark, green and semi-plastic.			
	29. Two hours after start of distillation, start adding N-690 slowly through 2" flexible line, no faster than is required to prevent charge from becoming granular.			

(Cont'd on Page 3.)

VAT	PAGE: 8 CODE: A-3-F LBS.	USE LBS.	N. CODE	ACCT.LBS.
	30. Fifteen minutes after fog disappears from mixer sight glasses, increase rate of N-690 addition as much as possible without permitting charge to become lumpy.			
	31. Immediately reset regulator to 10°C. and shut off heating steam.			
	32. Maintain vacuum while adding N-690.			
	33. Continue adding N-690 until total added in Steps 20 B through 33 is approx. 2 1-2 drums	1158	690	1158
	34. Shut off vacuum steam and condenser spray.			
	35. Start cooling water in mixer jacket.			
	36. Stop and open mixer.			
	37. Take two 4 oz. samples for duplicate moisture and solids determinations.			
	38. Immediately run in 1/2" layer of N-690 on top of charge and lock out drive motor. Record N-690.	———	690	———
	39. Deliver samples taken in Step 37 to laboratory.			
	40. If moisture is 0.5% or less, proceed.			
	41. Calculate N-690 required to adjust film solids to standard 40% value: (Actual solids____% ÷ 40%)-1.00=____Factor. ____Factor x 2000 -(N-690 Step 38) = _____N-690 to add.			
	42. When ready to pack batch, start mixer and run in N-690 calculated in step 41.	———	690	———
	43. Mix 10 minutes.			
	44. Stop mixer.			
	45. Pack out batch immediately through screen into 15 gallon drums (N-645) at 130 lbs. net.			

(A)A-3-F

FLUSHED PIGMENT N - FORMULA NOTES

A-3-F is a flushed "Dulux" dispersion of hydrous nickel (II) oxide, designated as "Polymer K" by the F&P Department. It is manufactured at Kenark, exclusively for F&P. The flushed product must be completely free of turbidity when reduced to enamel composition, applied as a .003" clearance film over black, and baked. Preparation of the aqueous Pigment N presscake used in the flushing process is described in the (A)A-2-P formula and notes.

OUTLINE OF FLUSHING PROCESS

The approximate weight composition of the flushed base product is:

A-2-P Pigment solids	300 lbs.	= 13.33%
N-693 RC-448 solids	150 lbs.	= 6.67%
N-694 RC-3078 solids	450 lbs.	= 20.00%
N-690 Amsco B solvent	1350 lbs.	= 60.00%
Total	2250 lbs.	=100.00%

Fifty percent of the A-2-P is charged into the 250 gallon Baker-Perkins vacuum mixer, slowly treated with all of the RC-448 resin solution (N-693) and then treated with RC-3078 resin solution (N-694) until the oil-in-water emulsion coagulates and reverses to water-in-oil, expelling breakout water which is decanted. The remaining half of the pigment presscake is added in five equal steps with breakout and decantation of water after each step. The remainder of the RC-3078 solution is then slowly added to the very viscous paste in the mixer, followed by 55 gallons of Amsco A solvent (N-692) and 11 lbs. of triethanolamine (N-695). Residual water is removed from the batch by vacuum distillation, the anhydrous base is reduced to the desired solids content by addition of Amsco B solvent (N-690), and the product is screened into shipping containers.

SCHEDULING

Because of the instability of A-2-P the strike and flushing schedules must be so integrated that the presscake is never more than one or two weeks old when flushed.

SPECIAL REQUIREMENTS

All safety regulations applicable to the flushing area and to the handling of petroleum solvents must be strictly enforced.

The most important tinctorial properties of Pigment N are extremely low strength and high transparency. The most exacting "Non-Bleeding" processing precautions must be extended to prevent contamination with any foreign material.

PERFORMANCE

Only two plant batches have been made to date (lots 10208 and 10271). Despite operational difficulties during vacuum distillation, resulting from limitations of the existing facilities, both batches were fundamentally satisfactory in initial properties and durability. Specific recommendations for action to eliminate the equipment difficulties have been transmitted to the Production Division in the writer's letter of 9-11-50 to J.H.Bailey, "Flushing Facilities - Building #12."

OPERATING NOTES

The "A" formula represents as firm a process as can be written on the basis of the very limited plant experience to date. Many of the details are tentative, as indicated below:

1. Batch Size

Due to scarcity of available pigment presscake, the two plant batches made to date were based on 265 and 280 lbs., respectively, of A-2-P rather than the 300 lbs. as formulated. The full 300 lb. charge can certainly be carried through the breakout and distillation stages without difficulty, but there is some uncertainty as to whether the final standardization volume will be too great to permit attainment of uniformity without use of a Lightnin Mixer.

2. Breakout Process - Steps 1-18

In all laboratory flushings (2.5 gallon mixer) in which A-2-P of normal solids content (26-30%) was employed, satisfactory performance was obtained by adding 70% of the total presscake for the first breakout, followed by three 10% stepwise breakouts. The presscake (7#910) used in the plant flushings was abnormally low in solids (21-23%) and very low in consistency, with the result that the 70-10-10-10 flushing sequence failed to build the consistency of the flushed mass up to the rather viscous state required to effect complete dispersion of the presscake in the resin. The modified sequence (50 followed by five 10's) completely corrected the dispersion difficulty, and has been incorporated in the "A" process. Upon establishment of optimum A-2-P press burden in the plant it should be possible to simplify the incremental flushing sequence to something like 70-15-15. It is believed to be important to attain a state of near-plasticity at the end of the breakout sequence in order to attain optimum pigment-resin dispersion. This, however, has not been proved by controlled experiment.

Approximately 65% of the total water in the batch is decanted. The remainder must be distilled. All decanted breakout waters are very turbid, as discussed below under "Coal Yield".

3. Predistillation Reduction - Steps 19-20

Addition of MC-3078 to the total 1:2 pigment:binder ratio prior to distillation has been specified by F&F. No opportunity has been obtained for investigating obvious economy measures involving alteration of the composition of the finished product or the sequence of addition of ingredients.

Addition of both the resin (Step 19) and the initial portion of solvent (Step 20) must be conducted sufficiently slowly to maintain a state of near uniform composition in the batch. If the very slow critical rate is exceeded longer than momentarily it is virtually certain that the batch will become lumpy and that it will remain non-uniform and lumpy throughout the distillation process. This condition is believed to be detrimental but no controlled experiments to check this point have been permitted to date.

4. Over-night Shutdown - Step 20.

Shutdown at the point indicated has no detrimental effect in the laboratory, provided the sides of the mixer are scraped down and the surface of the batch is covered with a thin layer of clear solvent to prevent skinning.

5. Triethanolamine Treatment - Step 22.

The quantity of triethanolamine used must not be varied without consent of F&F. Decreasing the triethanolamine in the final base tends to increase reactivity. Increasing the agent inhibits reactivity and improves dispersion, gloss and clarity, but also retards enamel drying rate and increases degree of darkening on baking. The agent is added prior to distillation, as specified by F&F. It is not known whether it would be more, or less, effective if delayed until near the end of distillation.

6. Vacuum Distillation - Steps 23-36.

The detailed directions represent the best apparent description of use of the present equipment. The object of this step is the removal of residual water from the batch by vacuum distillation of an azeotropic mixture of water and solvent. Excessive temperatures tend to gel the resin. Gelled material cannot be recovered. In the laboratory, the distillation proceeds smoothly and effectively, at 24-26 inches of mercury vacuum, if the mixer jacket is maintained at a temperature of 180°F.-190°F. by a constant supply of hot water. The batch is allowed to become progressively more viscous throughout the distillation. As the desired anhydrous condition is approached, the batch, which has been distinctly milky in appearance, abruptly becomes dark green and clear. Actual batch temperature ranges from 120 to 130°F. during distillation at the above pressure. Upon complete removal

of water from the batch (i.e., to the 0.5-1.0% range), the batch temperature promptly rises and fog disappears from the mixer sight-glasses. Best dispersion and clarity have been obtained by the writer when the charge has been permitted to reach a highly viscous, semi-plastic consistency at this stage. This condition cannot be risked, however, if the mixer jacket is heated only with high pressure steam (as has been true in the case of the plant mixer to date), because of the great risk of resin gelation; this occurred in the case of the first plant batch. Steps have been taken to provide the desired improvement in plant facilities prior to future manufacture.

Solvent must be added throughout the final stage of distillation, in sufficient quantity to maintain the charge in a smooth, non-granular state.

Upon completion of distillation the heat supply is replaced with cold water, and solvent is added to the batch as rapidly as possible without forming lumps of non-uniform product.

Experience gained in the course of the next three or four plant runs should permit much more precise specification of time-temperature cycles and of solvent addition times and rates.

7. Testing

The product is to be standardized at 39-41% solids content. Film solids are determined by drying a weighed sample of the mill base. Specifically, using an analytical balance throughout, weigh a 1/4 oz. pill box and lid, pour a thin film of the sample (±500 mg) into the pill box, replace lid, weigh, remove lid, place open pill box and weighed film in 110°C oven, reweigh with lid after 3 hours, and continue heating until weight is constant. Calculate percent film solids from respective net weights of wet and baked films.

Exposure series are now underway to establish maximum permissable moisture content. This is determined by the conventional toluene distillation method.

Clarity and transparency are the vital optical properties of Pigment N. Officially, these properties can be determined by reducing 50 g. of the mill base with 41 g. RC-103, adding 2 g. VC-1000 and 0.5 g. VM-7750, applying a 0.003" clearance applicator film over black, and baking 1 hour at 225°F. The baked film must be free from cloudiness. If desired, direct comparison can be made in this test against a pigment-free clear enamel. In practice, however, it is always possible to appraise the clarity of the product accurately by inspecting a sample of the mill base in a glass container or on a bright spatula. Bases of bright dark green masstone color and free of turbidity or milkiness are always satisfactory. No limit standards of turbidity have been established to date, and no arrangements have

been made with F&F for acceptance of cloudy bases. Although firm conclusions are impossible until further experience is gained, semi-works and plant performance to date lends support to the optimistic view that the incidence of cloudy production will be sufficiently rare to permit F&F to consume it, without difficulty, in selected applications.

8. Packing

In the two plant runs to date it has been necessary to remove lumpy undispersed tailings by screening the product through a 20 mesh screen supported below a discharge gate clamped to the decanting rim of the mixer.

Because of their availability, 15 gallon drums have been used as shipping containers to date. In the interest of economy it is desirable that arrangements be made with F&F for use of mutually satisfactory drums of larger size, preferably also suitable for use in shipping the ingredient resin solutions from Philadelphia to Newark.

GOAL YIELD

As indicated on page 1 of these notes, the theoretical commodity yield at 40% solids content, based on 900 lbs. solids input, is 2250 lbs. Decanted breakout waters, however, invariably are quite turbid, indicating obvious yield loss at this stage. This loss has been determined by analysis in the case of four laboratory runs to range between 1.7% and 3.6%, averaging 2.5%. The goal yield is, therefore, 2250 x .975 = 2194 lbs.

The estimated production yield, used in costing the process, is 1969 lbs., or 89.75% of the above goal. This yield is the actual average of the net pack yields of the total plant production to date corrected to standard batch size and solids content (2 batches, 1955 and 1983 lbs., respectively).

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10/10/50

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