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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

"AURIC BROWN", F-4-P - PROCESS STUDY

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

"AURIC BROWN", F-4-P - PROCESS STUDY

FEBRUARY - AUGUST, 1951

CHARGE: 1100-31-8

SUBMITTED BY: R. R. DENSLOW DATE SUBMITTED: 10/2/51

APPROVED BY : B. H. PERKINS 10/11/51 DATE ISSUED: 10/15/51

INTRODUCTION:

This report summarizes the results of a process study carried out on "Auric Brown", F-4-P during the period February - August 1951.

SUMMARY AND CONCLUSIONS:

The work was initiated as a result of complaints from F. & F. on the quality of F-4-P shipments, especially during 1950.

It has been shown that the poor quality of our shipments was due to the character of copperas used in manufacture. Specifically, material currently received from Edge Moor is considerably higher in manganese content than that used several years ago in our original work. This is the result of a change in titanium ore (Quilon to Trail Ridge).

Products which are satisfactory to Parlin have been made from Baltimore Copperas (high Mg, low Mn) and from Stanley Copperas (low Mg, low Mn). In the latter case it is necessary to add magnesium sulfate. Products of fair (border line) quality have been made from Edge Moor copperas (low Mg, high Mn) by adding magnesium sulfate and precipitating out the manganese with potassium permanganate.

An apparently satisfactory testing method has been developed in cooperation with Parlin.

New limit dry plate (masstone) standards have been set up. Indications are that products meeting these standards can be manufactured without difficulty.

A new plant formula ("D" process) has been written incorporating the information presented below. A summary of this process is attached as an appendix.

HISTORICAL - STATEMENT OF THE PROBLEM

The manufacture of F-4-P has been under the supervision of the Production Division since April 1948. At that time, ten batches had been made on a single formula and evaluated critically by Parlin. Seven were rated as satisfactory; two of the others were of borderline quality; one was definitely yellow and out of line in transparency.

Since then, a number of adverse comments have been received on shipments. During 1950, the complaints became more serious and the Chemical Division was requested to take up the problem again. Active work was started in February 1951.

Manufacture of the pigment had been carried out on the formula used in the above standardisation run and there was no evidence of deviations from the specified operating procedures.

Parlin's complaints have been based on their difficulties in matching their "Metallichrome" color families. Specifically, it was stated that our shipments of pulp when dispersed in single pigment

lacquers were usually too yellow and dull ("milky") in masstone. There were also indications of poor reproducibility. The evidence was somewhat confused but it was apparent that their difficulties were real and were largely the result of abnormal pigment quality.

Our work had two objectives:

(1) To determine definitely the type of product desired by F. & F. and to set up a testing method for evaluation purposes.

(2) To establish a manufacturing procedure for consistently producing material of the desired type.

Close cooperation with Parlin has been maintained throughout the work.

PATENT SITUATION:

The basic Parlin patent on flushed lacquers is U.S. 2140745 (R. T. Hucks). The use of hydrous ferric oxide of the F-4-P type is covered by U.S. 2335760 (also Hucks). The claims of this latter are for coating compositions; the general method for making the pigment is disclosed.

The Harmon (Vesce) "Rough Gold" patent is U. S. 2,384,579. The product claims cover coating compositions rather than the pigment.

In our opinion, nothing of a patentable nature has been developed as a result of the present study.

EVALUATION PROCEDURES AND SELECTION OF STANDARDS

The original "Metallichrome" color families were set up several years ago using a blend of semi-works F-4-P batches. To the best of our knowledge, these are still the goal standards. However, it appears that in some cases, compromise standards and some new shades have been set up by Parlin since then, using random batches of pulp; no details (lot numbers, etc.) are available at Newark.

All work on the problem of standardization and reproducibility has been complicated by two factors; (a) color drift and (b) inadequacy of testing methods.

Aged samples of pulp give enamels which are lighter and more opaque in masstone and redder in tint than enamels made from the fresh pulp. The redness is easily seen in a metallic and the opacity shows up as dullness of "milkiness" and lack of two-tone flash. The seriousness or even the existence of this drift was not known to either Parlin or ourselves until well along in the research program with the result that many of our early conclusions are open to question. Some drift occurs during processing of the pigment and immediately after manufacture;

however, it is ordinarily not too serious for a period of 3-4 weeks. Since little or no drift occurs in the lacquer vehicle, it is Parlin's practice to disperse the pigment into semi finished or finished lacquer as soon as possible after it is received. Aside from its effect on any stocking programs, the chief effect of color drift in our work is the impossibility of setting up a pulp standard for matching purposes and the consequent necessity for matching against panel standards of some type. Relatively little work has been done either in the past or during the recent study to reduce the amount of drift and it is uncertain whether or not it represents a workable problem. Its physical explanation is apparently a particle size growth.

The testing of F-4-P (experimental samples and plant production) has always been a serious problem and the methods used have been open to question either in respect to practical significance or reproducibility. The final test has been Parlin's ability to use the pulp to match the particular shades in which they are interested at the time. They have made use of a laboratory flushing technique which is quite time consuming; moreover, correlation of the results with those obtained in their plant has not been entirely satisfactory; this and the matter of reproducibility have been the subject of considerable discussion. Additional complications have been introduced by various changes in Parlin's plant dispersion technique.

As a guide in our work, considerable use has been made of a laboratory flush-out technique (in varnish) in which the tint is compared with dry plate standards. This was written up as TF-7007-1. This test is of some value in predicting, in a general way, what type of "metallic" will be obtained from a given pulp. It also has some value in intercomparing members of single laboratory series. However, it has occasionally failed in spotting batches alleged by Parlin to be unsatisfactory. Because of this and the obvious difficulties in correlating results with actual lacquer tests, the method has been abandoned except for certain research purposes.

As indicated above, Parlin has made various changes in their plant dispersion technique and in their laboratory dispersion methods. Of particular significance is the fact that their current criterion of quality is masstone color (lacquer). Metallics are made up only occasionally and then only to guide their plant color shaders.

At the beginning of the present study we were supplied with a new laboratory dispersion procedure for testing work. It involves flushing the pulp on a two roll mill in nitrocellulose/plasticizer, sheeting out and drying. The dried roll stock is stirred under specified conditions with the additional lacquer components (solvent, resin, etc.) and the resulting masstone lacquer sprayed to complete hiding on cardboard panels.

Sufficient work has been done to indicate reasonably good duplicability both between check tests at one laboratory and between tests carried out here and at Parlin. As a result of the work, Parlin

has set up new light and dark limit standard panels. These were made from single pigment lacquers prepared from the following recent batches of F-4-P:

Light limit : Lot 28450

Dark limit : Lot 28579

Products even darker than the "Dark limit" would probably be acceptable, if otherwise satisfactory in color. Parlin's chief objection is apparently to yellowness and dullness or "milkiness". Batches lighter than the "light limit" would normally give difficulty because of their opacity which is reflected in lack of "flash" when the lacquer is metallised.

Parlin has carried out some work fairly recently designed to cut the time required for testing by using forced drying to remove water from the roll stock. This tentative short method carries their code TM-69-B. Further work on this method is in progress.

Attempts were made (at Newark) to develop a laboratory dispersion procedure based on the use of a small amount (ca. 50g) of pigment. Flush-outs were made in 1/2 pint ball mills and the jars were subsequently rolled with the other lacquer ingredients. Products of good gloss were obtained but we were unable to match the depth of 2 roll dispersions (Ref. 1373-77).

SUMMARY OF LABORATORY PROCESS STUDY:

The work on lacquer testing, discussed above, was carried out concurrently with studies of miscellaneous process variables. In most of the latter, it was necessary to depend on spatula flushouts as described in TF-7007-1. Generally speaking, there was considerable irregularity in the results. If and when further work on this problem is required, a number of the experiments should be repeated, evaluating the results by lacquer tests. The major portion of the work, however, was concerned with the effect of impurities in copperas. In this case, the spatula flushout tests have been supplemented by lacquer tests and the conclusions are believed to be valid.

Copperas Quality - General

Copperas quality was investigated briefly some years ago in connection with the original development work on F-4-P. At that time, the chief impurities appeared to be titanium and magnesium. The latter was observed to have a powerful effect; however, since it was found to be present in batches of satisfactory tinctorial quality, no consideration was given to methods of removal or to detailed studies on the relation between amount of metal and color properties. The effect of titanium (normally present in duPont copperas to the extent of 0.2-0.3%) is similar to that of magnesium but much less marked. It appears to run fairly constant in amount and is ordinarily no cause for concern.

The recent work has confirmed the above but has shown that

certain types of copperas contain significant amounts of manganese as well.

F-4-P made in the laboratory from CP Copperas is very light and red in masstone (2 roll lacquer dispersion) and correspondingly opaque. This effect was checked in the plant using a rather pure commercial grade. This light, red material is unacceptable to F. & F.

As indicated above, magnesium has a powerful effect giving a dark masstone and correspondingly weak, yellow tint. As little as ca 0.05% of metal added as magnesium sulfate to CP copperas has a marked effect. To obtain standard color (see previous section), ca 0.4-0.5% (as Mg) is required. The mechanism of its effect is not known but is believed to be physical rather than chemical, resulting in a pigment of smaller particle size.

The effect of manganese is also marked. Like magnesium, it gives depth; however, the most noticeable result of its presence is dullness of the type regarding which F. & F. has complained. While as little as ca 0.02% of metal (as Mn) has a noticeable effect on color, satisfactory products can be made with as much as 0.05-0.06%. The upper limit of tolerance is not known; 0.15% is definitely too much.

It has been concluded that to make acceptable F-4-P, the copperas must contain a fairly high percentage (0.4-0.5%) of magnesium and as little manganese as possible, say, 0.06% maximum. Titanium in normal amounts (0.2-0.3%) is unobjectionable. Presumably the pigment used in setting up Parlin's original standards was made from copperas of this type.

Commercial Copperas

Because of a change in titanium ore (Quilon to Trail Ridge), the composition of Edge Moor copperas (N-391) differs from that made prior to circa 1950. Current material contains about 0.1% Mg and 0.16-0.18% Mn. From the above, it is obvious that this will give light, dull pigment.

Current Baltimore copperas (N-724, formerly N-391-S) is high in magnesium (0.2 - 0.5% Mg) and low in manganese, 0.05% Mn. All batches made from Baltimore copperas have been satisfactory. Since few analytical data are available, it is being recommended that for the immediate future, shipments be analyzed and the magnesium content adjusted by adding magnesium sulfate in the strike.

Several plant batches were made from Stanley Copperas (N-391-SS), a pure grade low in both magnesium ($< 0.05\%$ Mg) and manganese (ca 0.05%). By adding a sufficient quantity of magnesium sulfate this has given satisfactory pigment.

A sample of copperas was received from National Lead. This was high in manganese and was therefore given only very limited attention.

Purification of Copperas

The present filtration procedure for N-24 liquor removes most of the titanium but does not remove magnesium or manganese which are present as soluble sulfates.

No method is known for removing magnesium aside from recrystallization. There have been indications that it may be possible to counteract its effect by adding sodium fluoride. Additional work would be required to establish amount and the optimum procedure. Since the amount of magnesium required is relatively high, the problem of its removal is not believed likely to arise.

Two methods for the removal of manganese have been investigated. The first involves oxidation of the manganese with lead peroxide after oxidation of the iron has been completed. A dark colored sludge (MnO_2 ?) is formed but the main reaction is the following:

$$2\ MnSO_4 + 5\ PbO_2 + 3\ H_2SO_4 \rightleftharpoons 5\ PbSO_4 + 2\ H_2O + 2\ H\ MnO_4$$

The permanganate formed should be unobjectionable. Because of cost considerations, more work has been done on a second method, namely adding potassium permanganate to the oxidized iron solution.

$$3\ MnSO_4 + 2\ K\ MnO_4 + 2\ H_2O = 5\ MnO_2 + K_2SO_4 + 2\ H_2SO_4$$

Separation of the solution from the major portion of the sludge presented no great difficulty in the laboratory and both methods appeared to work satisfactorily (in the laboratory) with Edge Moor copperas. The second method was tried with fair success in the plant. However, with existing equipment, considerable sludge ran into the strike vat. Possibly because of this, the resulting pigment was of borderline quality, being slightly dull. It is probable that a satisfactory purification procedure might be worked out but additional equipment might be required.

Miscellaneous Variables

Normally, no difficulty is encountered in oxidizing the iron with the specified amount (10% of theory) of chlorate. With the theoretical amount, a slight test for Fe^{++} was obtained but the pigment was normal. A large reduction (to 85%) in chlorate gave a dark product, presumably ferroso ferric oxide. At an intermediate point (93%) a very red product, resembling Mapico Red rather than F-4-P, was obtained. It is recommended that the present (107 %) figure be retained.

Sodium pyrophosphate (e.g. 1#/mol. copperas) added to the iron or soda ash gave very dark yellow material.

The effect of sodium fluoride in giving light, red pigment has been mentioned above. The experiments with this material gave rather

irregular results. Further work is indicated especially in respect to the effect of sodium fluoride on magnesium and manganese.

Some additional work has been carried out on the effect of the iron/soda ash ratio as judged by the pH of the slurry. Increasing the pH from 7 to 7.5-8.0 gave a lighter masstone. Reducing it to 5.5 gave a considerably darker masstone. It is recommended that the present practice of adjusting to pH 7.0 after the strike be continued.

PLANT STUDIES:

Four plant runs of five batches each were followed and tested in lacquer. In most cases tests were made both at Newark and at Parlin. Agreement between the results, while not perfect, was fairly good and was considered satisfactory.

The procedures used are indicated in Table I which should be self-explanatory. Three of the batches were made by standard formula using Edge Moor copperas (N-391). They all showed the masstone dullness regarding which Parlin has complained and which is characteristic of products made from high manganese copperas. The batches made from Baltimore copperas (high Mg, low Mn) were all satisfactory although one (28450) was unexpectedly light; this material represents the new light limit standard. Stanley copperas (low Mg, low Mn) used "as is" gave a light red product similar to what is obtained with CP material. By adding magnesium sulfate to approximate the composition of Baltimore copperas, satisfactory products were obtained.

The attempts to remove or inactivate the manganese in Edge Moor copperas by permanganate treatment after oxidation were only partly successful. Lot 27898 was quite light presumably because of insufficient magnesium or possibly because of the bisulfite which was added after the strike to remove MnO_2 . Bisulfite was not added in the later runs since laboratory work indicated it to serve no useful purpose; the sludge was allowed to settle and an attempt made to keep as much as possible from running into the strike vat. In these later runs, the masstone depth was satisfactorily adjusted by adding magnesium sulfate; however, they were all slightly dull compared with the standards or batches made from Stanley copperas plus magnesium sulfate. Additional work would obviously be required to develop an entirely satisfactory process based on the use of Edge Moor copperas.

As mentioned above, Parlin stated that the color of lot 28450 was satisfactory as a light limit standard. At the same time, lot 28579 (also from Baltimore copperas) was selected as a dark standard. It was indicated that material even darker than lot 28579 would be acceptable provided that it was not lacking in intensity.

Observations made during these plant studies indicated the making operation to be under good control. The batches made early in May showed evidence of slight contamination in the press room and one batch (27688) was returned on this account. Improvements made in the clean-up procedure have apparently corrected this condition.

TABLE I

F-4-P

PLANT BATCHES MADE UNDER CHEMICAL DIVISION SUPERVISION

MAY - AUGUST 1951

Lot	Date	Formula	Quality	(Lacquer Masst
27688	5/9/51	Control - Edge Moor Copperas	NG	O.K. depth but d
27739	5/10/51	Balt. Copperas	OK	
27791	5/11/51	Stanley Copperas (as is)	NG	Too light and re
27795	5/14/51	Like 27688. Production Supervision	NG	Dull & light
27898	5/15/51	E.M. Cop. plus K MnO_4/$NaHSO_3$	OK	but light
28377	5/29/51	E.M. Cop. Like 27688	NG	Lt. & dull (milk
28392	5/31/51	E.M. Cop. plus K MnO_4/$MgSO_4$(65# N563)	NG	Lt. & sl. dull
28450	6/1/51	Balt. Cop.	OK	but light.(Borde
28562	6/5/51	" "	OK	
28579	6/6/51	" "	OK	
29872	7/23/51	Stanley Cop. plus $MgSO_4$(315# N563)	OK	
29892	7/24/51	"	OK	Borderline (ligh
29920	7/25/51	"	OK	
29904	7/26/51	E.M. Cop. + K MnO_4/$MgSO_4$ (1)	OK	sl dull vs. 2987
29934	7/27/51	" (1)	OK	" " "
30624	8/27/51	Stanley Cop. plus $MgSO_4$ (2)	OK	
30669	8/28/51	" (2)	OK	(Dark)
30646	8/29/51	" (2)	OK	
30686	8/30/50	E.M. Cop. + K MnO_4/$MgSO_4$ (3)	OK	Dark, sl dull. B
30710	8/31/51	" (3)	OK	Dark, sl dull. B

(1) Like 28392 but N-563 increased to 300# for greater depth
(2) Like 29872 etc. but slight increase in N-563 (to 325#)
(3) To check 29904, 29934
(4) This lot was returned by Parlin because of slight contamination with red pig
(5) Our test. Not evaluated by Parlin. Better than 28377 but of borderline quali

FUTURE WORK:

On the basis of the work covered in this report, a new F-4-P process ("D") has been written and submitted to Quality Control. The Production Division will be asked to resume supervision of the process.

No laboratory work, aside from testing plant batches, has been carried out since June and no additional work is contemplated for the present. Should it be necessary to take up work at some future date, attention might well be given to the following:

Further studies on copperas purification. (Removal of Manganese)

Further studies on physical variables during manufacture, for example temperature, strike time, agitation, concentration, digestion, washing, water content of pulp etc. A number of experiments along these lines have been carried out but with inconclusive results, possibly due to inadequate testing methods.

Effect of foreign ions (fluoride, chloride, miscellaneous cations) during the strike.

Seeding - Possible effect of material from previous batch. Intentional addition of seed material.

Surface treatments.

REFERENCES:

Details of the experimental work are recorded in Notebooks 1373 and 1402 and in DSN 51-31.

Progress reports will be found in the Inorganic Monthly Summaries beginning with February 1951.

Reports on various discussions with Parlin will be found in the following Technical Service Reports:

WFS (#5)	2/12/51
ECB (#10)	2/27/51
WFS (#23)	5/16/51
WFS (#24)	5/22/51
WFS (#33)	6/25/51
WFS (#39)	7/20/51
RRD (#1)	8/15/51
WFS (#43)	9/18/51

Correspondence on Copperas:

Moomaw - Perkins	4/24/51
Moomaw - Perkins	6/7/51
Hageman - Smith	6/11/51
Bowles - Cantwell	6/20/51

Establishment of Standards:

H. L. Priddy/R. O. Isele - Spengeman 8/3/51
See also TSR WFS #43, above

Testing method:

Letter: Spengeman - Andrews, 2/7/51 and attached
Letter: Isele - Spengeman

RRD:lg
Att.

APPENDIX

F-4-P - "D" PROCESS

The following is a summary of the D process which should be consulted for details. It differs from the "C" process in that the use of Baltimore copperas is specified and provision is made for maintaining the magnesium and manganese content within definite limits.

Batch Size: The estimated yield is 2133 lbs. This is based on the assumption that half the petronate used is retained in the pulp.

Ingredients:

6250# Baltimore Copperas. (Total iron expressed as $FeSO_4.7H_2O$), N 724

Manganese (as Mn) 0.06#/100# $FeSO_4.7H_2O$ (max.)
Magnesium (as $MgSO_4.7H_2O$) ca 200-300#/100# $FeSO_4.7H_2O$

1191# Sulfuric Acid (100%), N 27

428# Sodium Chlorate, N 12

(ca.) 25# Magnesium Sulfate, $MgSO_4.7H_2O$, N 563

3800# Soda Ash, N 3

100# Petronate, N 490

Procedure:

Approximately the desired amount of copperas is dissolved in 283 vat and the volume of solution noted. A sample is analyzed (#/gal.) and the total weight of $FeSO_4.7H_2O$ in 283 vat adjusted to 6250# by adding additional N 724 or by removing a calculated amount of solution. Magnesium sulfate N 563 is added if necessary to a total of 325#/batch.

After adjusting to a specified volume, oxidation is carried out by adding sulfuric acid and sodium chlorate and heating to 180°F.

Soda Ash is dissolved in 182 vat and heated to 180°F. (Prior to use, the vat is thoroughly cleaned.)

Precipitation is carried out by running the iron solution into the soda ash solution in 182 vat. 75% is added in 30 minutes and the remaining 25% in 90 minutes.

After the strike, the pH of the slurry is adjusted if necessary to 7.0 (soda ash or sulfuric acid), the petronate added and the batch stirred 45 minutes before pressing.

The pulp is washed in the press to 1,000 ohms.