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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: RT-455-D
"WATCHUNG" RED B (RESINATED)-Manufacture in #9 Bldg.
1. Correct light masstone-yellow tint tendencies.
2. Correct difficulty with increased fires on grinding.
3. Develop blue tint variable.

Period Covered: March - May 1949

Charge: BCK-32 (1100-31-32)

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RT-455-D

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1. Correct light masstone-yellow tint tendencies.
2. Correct difficulty with increased fines on grinding.
3. Develop blue tint variable.

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Charge: BCN-32 (1100-31-32)

SUBMITTED BY: E. J. HESS E. J. Hess DATE SUBMITTED: 5-23-49

APPROVED BY: J. O. MORRISON J. O. Morrison May 24, 1949 DATE ISSUED: 5-31-49

INTRODUCTION:

Plant difficulty with RT-455-D manufacture involving accumulated production of approximately 10,000 lbs. of yellow tint substandard, which was also predominantly light in masstone, made it necessary to issue a Plant Assistance work request in March, 1949.

Laboratory and plant study (#9 Building) was started immediately to correct the following deficiencies of the modified formula in use in the new #9 Building unit;-

1. Correct the increased pigment fire hazard during pulverization, apparently resulting from #9 Building manufacture.

2. Correct lightness of masstone and yellowness of tint, and develop a variable that could be depended upon to give blue tint whenever desired.

SUMMARY & CONCLUSIONS:

Rebaking (for 12-16 hours at 180°F) of a number of samples from current light-yellow substandard effected some increase in depth of masstone and a decided increase in blueness of tint. Approximately 3000 lbs. of very light and yellow substandard was converted to a more easily shadeable product by this means.

Laboratory work indicated a maximum of 1. mol % Tobias Acid as an "accessory" in the Red 2B acid diazo to be an effective variable for blue tint manufacture. Darker, somewhat duller masstones were also obtained. Bleed in alcohol, hot and cold water, acetic and sulfuric acids are not affected to any extent, if the maximum limit specified is maintained.

Meanwhile, it was found that in #9 Building manufacture a dark, blue tint product could be obtained with the proper variable combinations even without the use of the Tobias Acid "accessory". The variables used consisted of a 25% increase in the sodium rosinate, an approximate 30% cut in the BON slurry volume before coupling, a slight increase in coupling pH (pH 8.6-8.9 instead of 8.5-8.6) and a 16 hour baking period for the lump. There was some difficulty in maintaining masstone on the dark side of standard due to over-development during filtration (slurry not quenched after heat development). Quenching to about 145°F corrected this light masstone tendency but at the expense of an increase in yellowness of tint.

The fire hazard apparently resulting from the use of #9 Building equipment (2 batches - 2 grinding fires of unknown origin) did not seem to be the result of non-standard processing and handling of the rosinate solution, as use of a special non-precipitating sodium rosinate solution did not solve the fire problem. It was observed that

the intensive agitation obtained in the [illegible] Building coupling vat during the mixing of the concentrated BON and sodium resinate solutions resulted in the considerable aeration of this mixture, which might interfere with the desired formation of the less inflammable calcium resinate when the precipitant was added (just before coupling). In an attempt to overcome this effect the BON solution was diluted to five times the standard volume before adding the resinate. This change together with careful control of mill temperature during grinding apparently had solved the fire problem.

Recommendations for control of quality of [illegible]-D manufacture in [illegible] Building were issued for inclusion in the formula notes and the Production Division assumed supervision of manufacture in May, 1949.

DISCUSSION:

Rubbing of a number of samples from current very light and yellow production indicated that some increase in depth and a definite increase in blueness of tint could be obtained by reducing this material. [illegible] was [illegible] at [illegible]°F. Of the [illegible] lbs. processed to date, [illegible] lbs. finished [illegible] straight and the remainder improved considerably (particularly in tint) so that it was readily shadeable with [illegible] - [illegible] production.

The formula used in this study was a modification of the basic [illegible] Building [illegible] process (dated 1-17-49). The principal changes were:

1. Use of the [illegible]-D dissolution procedure (higher concentration [illegible] of the [illegible] [illegible] prior to addition of the [illegible] [illegible] standard [illegible] procedure [illegible] [illegible] [illegible]). This method apparently gives more complete dissolution and better yields on large scale operation than the [illegible] [illegible] technique.

2. Use of a "[illegible]" resin solution method (increased [illegible] ratio, slightly more concentrated volume) in an attempt to lower the increase in fire hazard during pulverization apparently resulting from [illegible] Building operation.

In spite of [illegible] of the resin solution variable a fire of unknown [illegible] [illegible] [illegible] of the above process. More anti-fire precautions were then taken. These included:

1. Observation had indicated that excessive foaming and bulking occurred in the concentrated BON-sodium resinate solution mixture which might interfere with satisfactory conversion of the sodium resinate to the less inflammable calcium salt. Accordingly, the BON solution was diluted approximately five-fold ([illegible] gallons to [illegible] gallons) prior to addition of the sodium resinate and the calcium chloride.

2. Special precautions were taken in drying and grinding, i.e. delivery of the lump to the grinder at a maximum temperature of 100°F., and establishing of a maximum permissible mill temperature during grinding of 130°F.

There was no further difficulty with fires and these steps were incorporated in the basic #9 Building procedure.

Observations of the condition of the BON, calcium salt-calcium resinate slurry in the #9 Building coupling vat prior to coupling indicates a considerable bulking of the slurry without necessarily exhibiting a normal foaming condition (bubbles). A comparison of a stick measurement and the manometer figure (which is based on weight of liquid in the vat) ordinarily shows a 35% increase for the stick over the manometer figure. This same effect may be obtained in #6 Building operation, although probably to a lesser extent because of the less [illegible] agitation. In any case, use of #6 Building coupling and develo[illegible] volume data with manometer volume control in #9 Building probably results in appreciably higher actual volumes and may account for part of the difficulty with light masstones in #9 Building RT-455-D manufacture.

As the principal requirement at the time this study was started was dark masstone-blue tint material for shading, all the variables used were based on #6 Building experience in obtaining a product of this type. These included:-

1. A 25% increase in rosin to obtain depth of masstone.

2. Increased development pH to obtain masstone depth. The pH was increased from a standard pH 8.3-8.5 to pH 8.6-8.9. Five to ten pounds more of caustic soda should give the desired test.

3. Decreased coupling and development volumes as measured by the manometer were used to obtain darker masstone. BON volumes before coupling ranging from the standard 9700 gallons to 6100 gallons were used. The lower volume apparently also gives definitely bluer tint.

4. Increased baking time at 180°F to obtain depth and blueness. Indications are that the standard 8 hour period at 180°F is not quite enough to guarantee maximum depth of masstone and blueness of tint. An increase to 12-16 hours is recommended.

5. Quenching of the color slurry after heat development prior to filtration. Observation of a number of batches indicated a definite loss of depth between vat control and lump samples. Indications are that this is due to over-development while filtering. There is some possibility, however, that quenching may give an undesirable increase in yellowness of tint.

Variables used and the results obtained during this study follows:-

1. The basic #9 Building formula gave a light-ok-vs to s. yellow product.

2. Combining the 25% increased rosin, a BON volume of 6400 gallons, a baking time of 16 hours and omitting the blanc fixe addition (for requested increased strength) gave a desirable dark - 9% strong - blue product. This batch with about one-third of the first batch was blended with 1400 lbs. of substandard stock to give a satisfactory 2900 lb. mix.

3. A second batch made on a similar formula except that the blanc fixe was added after heat development also finished on the dark-blue side of standard. An undesirable dullness of masstone obtained in this case was believed to be due to an error (omission of some of the acid from the diazo) which resulted in a high coupling pH (pH 10.5 instead of 8.0-8.5).

4. Combining the 25% increased rosin, a baking time of 16 hours, a BON volume of 7500 gallons and a development pH of 8.6-8.9 gave a light-ok-vs dull product. The blanc fixe was added in the standard manner (before coupling) in this case.

5. Combining the 25% rosin increase, the baking time of 16 hours, the BON volume of 6500 gallons, the increased development pH of 8.6-8.9 and the quenching after heat development gave a dark-yellow product. The quenching apparently prevented masstone lightening but at the expense of increased yellowness of tint.

Meanwhile, laboratory work had been undertaken to develop a blue tint variable. PTMSA and PCAOSA (Red 2YLN base) added in 5.0 mol % amounts as diazo "accessory" intermediates were not very effective. Small amounts of Tobias Acid, however, (0.5 to 3.0 mol % additions) increased blueness of tint considerably. Bleed tests (alcohol, hot and cold water, sulfuric and acetic acids) remained satisfactory up to a maximum usage of 1.0 mol % Tobias Acid. At the 3.0% level alcohol bleed was worse than control. Fadeometer light stability was not affected by the use of the "accessory" intermediate. A definite increase in masstone depth and a slight increase in dullness also results from the use of the recommended maximum (1.0 mol %) of "accessory".

Notes covering the recommendations for the control of RT-455-D quality in #9 Building manufacture follow:-

The #9 Building process on which the recommendations are based differs from the 2.22 mol process originally designed for

#9 Building (dated 1-17-49) as follows:-

1. Use of the RT-618-D diazotisation procedure (higher concentration and solution temperature of the Red 2B sodium salt; precipitation of the Red 2B sodium salt solution with acid prior to cooling and addition of the sodium nitrite for diazotisation. In the orthodox RT-455-D process the solution is cooled, the nitrite added, and finally the the acid.) The new procedure apparently gives more complete diazotisation and, consequently, better yields on large scale operation than the old process. The necessity for analysing the Red 2B sodium salt solution in the vat is also thereby eliminated.

2. Due to an apparent increase in color-fire hazard resulting from early #9 Building operation, the sodium rosinate solution is now made by the so-called "non-precipitating" method.

3. The excessive foaming and bulking of the BON solution-rosinate mixture when made in the normal manner (low volume) might result in increased fire hazard due to incomplete conversion of the rosin to the calcium salt. For this reason the BON solution volume is increased from approximately 800 gallons to 4000 gallons prior to addition of the sodium rosinate solution.

4. Special precautions are specified for drying and grinding: delivery of lump color to the grinder at a maximum temperature of 100°F and establishment of 180°F as the maximum permissible mill temperature during grinding.

5. The time for baking the dried lump is increased to 16 hours to insure maximum depth of masstone and blueness of tint.

6. Seventeen pounds of Octanol (N-588) are added before heating to reduce foam during heat development.

The following summarizes the variables recommended for controlling RT-455-D manufacture in #9 Building. No attempt is made to supply an "OK straight" formula for the present but experience with the suggested variable combinations may point out the proper approach to the problem. The procedure on which these suggestions are made is based on the modified #9 Building formula described above.

<u>For light masstone-yellow tint.</u>-

Basic process but bake only 4 hours at 180°F.

<u>For light masstone-OK to s.yellow tint.</u>-

Basic process.

<u>For light masstone-blue tint.</u>-

This is a tentative procedure and never has been tried in the plant. Some depth and dullness of masstone may result from the use of the "accessory" amine. Laboratory tests indicate that

sulfuric and acetic acid, hot and cold water, and alcohol bleeds are satisfactory but these should be checked on the first plant trial.

Basic process but:-

a. Use 1% "Lithosol" Acid TOB (N-88) as an "accessory" in the diazo (486 lbs. N-467 plus 5 lbs. N-88). It is inadvisable to use more than 1% N-88 because of probable bleed.

b. Bake at 180°F for 8 hours only.

For dark masstone-yellow tint,-

This is a tentative procedure never tried in the plant.

Basic process but:-

a. Use M Gum Rosin (N-312) to replace K Wood rosin (N-239).

b. Increase rosinate amount 25% (280 lbs. N-312-37-1/2 N-7 100% in 280 gallons).

c. Increase development pH to 8.6-8.9 (requires additional 5-10 lbs. caustic soda 100% after coupling).

d. Quench slurry after heat development.

For dark masstone-OK to s.yellow tint,-

This has not been tried in the plant.

Basic process but:-

a. Increase rosinate amount 25% (280 lbs. N-239-37-1/2 N-7 100% in 280 gallons).

b. Increase development pH to 8.6-8.9 (requires additional 5-10 lbs. caustic soda 100% after coupling).

c. Decrease volume of BON slurry just before coupling from 9680 gallons (98" Vat 902) to 8420 gallons (85" Vat 902).

d. Quench slurry after heat development.

For dark masstone-blue tint,-

A process similar to that suggested for dark masstone-OK to s.yellow tint, except for elimination of the quenching step, has given dark-blue and light-OK material in two trials.

A suggested procedure which has not been tried in the plant but which should give more dependable performance follows:-

a. Use up to a maximum of 1% "Lithosol" Acid TOB (N-88) as an "accessory" in the diazo (486 lbs. N-467 plus 5 lbs. N-88).

b. Increase rosinate amount 25% (280 lbs. N-839 - 37-1/2 N-7 100% in 280 gallons).

c. Decrease volume of BON slurry just before coupling from 9680 gallons (98" Vat 902) to 8420 gallons (85" Vat 902).

d. Increase development pH to 8.6-8.9 (requires additional 5-10 lbs. caustic soda 100% after coupling).

e. Quench slurry to 160-170°F after heat development.

Observations based on #9 Building manufacturing experience,-

1. Manufacture in #9 Building appears to average much lighter in masstone than #6 Building production.

2. Quenching after heat development appears to cut down this light masstone tendency but apparently at the expense of a slight increase in yellowness of tint.

3. Volume adjustment for the BON slurry prior to coupling must be based only on manometer readings. If a measuring stick must be used, the formulated volume measurements must be increased by 35%. This slurry bulking phenomenon, if present in the #6 Building operation to any extent, may partly account for the tendency of #9 Building manufacture to go light in masstone (see above). #6 Building stick measurements (e.g. 100") were translated directly to #9 Building manometer measurements (100") with a possible increase in actual volume of as much as 35%. Increased coupling volume is an effective variable to obtain light masstones in RT-455-D.

PATENT SITUATION:

There is no patent restriction in the manufacture of RT-455-D. It is not believed that this study has resulted in any patentable developments.

GLOSSARY:

RT-455-D - The rosinated calcium salt of the coupling of Red 2B acid diazo and Beta hydroxy naphthoic acid. About 16% of calcium rosinate and 9.2% of blanc fixe are present in the finished toner.

Red 2B Acid - Ortho-chlor-meta-toluidine-para-sulfonic acid.

PTMSA - Para-toluidine-meta-sulfonic acid.

PCAOSA -Para-chlor-aniline-ortho-sulfonic acid.

Tobias Acid - Beta naphthylamine-1-sulfonic acid.

BON - Beta hydroxy naphthoic acid.

EXPERIMENTAL DETAILS:

DSN-49-21.