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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

BARIUM LITHOL RED TONERS, RT-364-D and RT-364-DR.
FINAL PLANT STANDARDIZATION OF THE ECONOMY PROCESS
FOR RT-364-D ("A" PROCESS).

DEVELOPMENT OF RT-364-DR FOR RUBBER USE.

DEVELOPMENT OF A DRY MIX ECONOMY STANDARD FOR
Period Covered: RT-364-D ("B" PROCESS).

SEPTEMBER, 1945 - FEBRUARY, 1948.

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(B Process).**

SEPTEMBER, 1945 - FEBRUARY, 1948.

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INTRODUCTION:

The decision to discontinue the manufacture of colors using mixtures of rosinate and naphthenate because of patent restriction made it necessary to revise the standard economy process for RT-364-D, K-2057. It was therefore decided to restandardize this product using blanc fixe as the exclusive strength standardization component, replacing the 5% blanc fixe - 5% barium rosinate combination previously formulated.

Subsequent to the restandardization work difficulty with poor resistance to the curing process in the rubber test with the economy type material and finally quality difficulties in paint and ink made it necessary to return to the original K-1597 manufacturing process.

SUMMARY & CONCLUSIONS:

This development problem began as a straightforward restandardization job designed to replace the barium rosinate-blanc fixe extending ingredient mixture (used in the K-2057 process) with all blanc fixe. The barium rosinate was originally used at the request of the Sales Division in their attempt to maintain the use of blanc fixe in toners at a 5% maximum.

Plant batches made using the K-2057 process (except for the substitution of the blanc fixe for the rosinate) were all dark and dull in masstone and blue in tint versus the RT-364-D standard, lot 43564. Most of this difficulty was probably a result of raw material variation (particularly of the Tobias and Naphthenic acids) plus the fact that the standard, lot 43564, represented selected material that was somewhat lighter and more intense in masstone than was normally obtainable with the economy process (this was done to meet competition). Indications were that a slight dulling effect resulted from the elimination of the barium rosinate.

Increasing the sodium acetate buffer in the coupling from 0.4 mol per one mol coupling to 1.1 mols and lowering the formulated development pH range from 9.5-10.5 to 9.3-9.7 gave some improvement but it was finally necessary to restandardize on the dull masstone, slightly blue tint side of standard lot 43564.

A formula corresponding to the process used for the components of the new RT-364-D standard, lot 49274, was issued as the RT-364-D standard formula, K-2439, replacing K-2057.

Meanwhile, during the course of the evaluation work, it was found that the economy process material (that is, both standard lots 43564 and 49274) showed poor resistance to cure in the rubber test with the result that the panels obtained were much lighter and yellower than those secured with the previous high cost standard, lot 32404, and with current competitive material. The possibility that the naphthenic acid was responsible for the poor results in rubber was considered but tests made on previous plant manufacture using Turkey Red Oil to replace the naphthenic acid (see KN-45-90) were of the same poor quality.

Finally it was decided that because of the low volume of sales for rubber use the high cost standard, lot 32404, should be re-instated as the RT-364-DR standard for rubber and the K-1597 formula was re-issued as the RT-364-DR standard process, K-2474.

Supervision of manufacture of RT-364-D and RT-364-DR was accepted by the Production Division in April, 1947.

Meanwhile, because of poor masstone performance (dullness) of the K-2439 process, a sick list work request was issued in September, 1947. After some discussion it was decided that because of the comparatively low sales volume of RT-364-D and because of the probable considerable research time necessary it was decided to manufacture RT-364-D for all uses on the RT-364-DR, K-2474, process. Laboratory mixes had shown that current manufacture for rubber could be shaded with approximately 12% RT-431-D and 10% blanc fixe to match the RT-364-D standard, lot 49274. A slight cost saving also was obtained with the dry mix process compared with K-2439 (now designated RT-364-D(A)).

Subsequently, in February 1948, a dry mix process, RT-364-D(B), was issued replacing RT-364-D(A) and the problem was closed out.

DISCUSSION:

The first process used in the restandardization work differed from K-2057 only in the fact that 60 pounds per mol of blanc fixe was added to the beta naphthol solution prior to precipitation with acid. This was expected to eliminate the necessity for blending the finished ground material with blanc fixe and barium rosinate as previously formulated.

Manufacture was started in September, 1945; a series of five batches were made. All of this material was dark and dull in masstone and blue in tint versus standard, lot 43564, and was deemed unsuitable for a new standard. Experiments with high air velocity drying of RT-364-D with these batches indicated that satisfactory quality and more rapid drying could be obtained with the new dryers.

Starting in November, 1945, a revised procedure designed to correct masstone and tint deficiencies were used in RT-364-D manufacture. The changes introduced included:

1. Replacement of the acetic acid-hydrochloric acid mixture used for precipitating the beta naphthol before coupling with all acetic acid. By this means the buffer salt (sodium acetate) present during the coupling was increased from 0.4 mol per mol batch to 1.1 mol.

2. Lowering of the development pH from 9.5 - 10.5 to 9.3 - 9.7. This was done by decreasing the caustic soda for coupling from 66 pounds per mol to 63 pounds and/or by adjusting the coupling pH with acid or alkali prior to heat development.
3. Addition of the diazo to the beta naphthol slurry on the surface in an attempt to speed up this addition. An equipment change had resulted in a slowing down of the maximum possible rate for this process from 6 min. to 12 min. Although no coupling takes place at this point, previous experience with "acid coupling" formulas indicates that best quality results are obtained if the addition and stirring time of the acid diazo-beta naphthol mixture is held to a minimum.

Thirty-five batches were made during 1945 and 1946 using various combinations of the above variables. Average tint and strength performance improved to some extent during this period, masstones were closer to standard in depth but still remained dull versus standard, lot 43564.

Six batches made during this period were blended to give the proposed standard, lot 49274, which was submitted for evaluation in October, 1946. Evaluations were finally completed in April, 1947, and Sales accepted lot 49274 as the RT-364-D standard for ink and paint during the same month.

Comparisons of lot 49274 versus the original economy standard, lot 43564, and against the regular standard, lot 32404, follows:

Varnish dryer rubout:

Lot 49274 vs lot 43564: dull - OK - OK - OK
Light Stability: NT - equal. Tint - equal.
Lot 49274 vs lot 32404: dark - s.yel. - vvs strong - s.blue
Light Stability: NT - vs worse. Tint - vs worse

Rubber Test

Lot 49274 vs lot 43564: equal
Lot 49274 vs lot 32404: light - yellow

Examination of the rubber results showed that both economy lots were equal to lot 32404 on the uncured rubber panels but drifted light and yellow during the curing process. Examination of the competitive products, Imperial's X-1095 (C #48395), and Sherwin Williams Graphic Red CP-918 (C #48242), showed that they were essentially equal in tinctorial curing stability to the standard, lot 32404, and superior in this property to lot 49274.

Meanwhile, while the evaluation work was continuing, sixteen batches were made during January, 1947. Performance was fairly satisfactory versus the proposed standard, lot 49274, but there still remained a tendency toward the manufacture of slightly dark and dull masstone, slightly blue tint products.

In January, 1947, a new standard formula corresponding to the process used for the components of lot 49274 was issued as RT-364-D, K-2439 (subsequently the "A" process). K-2439 differed from K-2057 as follows:

1. Acetic acid only is used to neutralize the beta naphthol solution prior to coupling to replace a mixture of acetic and hydrochloric acids. The sodium acetate present during coupling was thereby increased from approximately 0.4 mol to 1.1 mol per mol batch.
2. The caustic soda for coupling is cut from 66 pounds to 63 pounds.
3. The pH before heat development is adjusted to 9.3-9.7 instead of 9.5-10.5.
4. The mixture of 30 pounds blanc fixe and 30 pounds barium rosinate added by dry mixing in K-2057 to adjust strength is replaced by 60 pounds blanc fixe added to the struck slurry just before heat development.

Evaluation work was continued in an attempt to develop a possible lead to correct the rubber curing problem. In order to check the possibility that the presence of naphthenic acid was responsible for the difficulty, two batches made during 1944 (lots 19563 in which Turkey Red Oil was substituted for the naphthenic acid during a naphthenic acid shortage period and lot 19970 made with naphthenic acid) were tested in rubber and found unsatisfactory in resistance to cure.

Finally, in March 1947, it was proposed that lot 49274 be set up as the regular RT-364-D standard for paint and ink. At the same time it was decided that lot 32404 be retained, temporarily, as a standard for a special rubber color designated RT-364-DR. K-2474 (subsequently designated the "A" process), which is similar to K-1587, was then issued as the RT-364-DR standard formula.

Upon acceptance of the two standards by Sales, the Production Division accepted supervision of manufacture of RT-364-D and RT-364-DR in April, 1947.

Meanwhile, because of the dull masstones (versus lot 49274) being obtained with the K-2439 process, a work request was issued in September, 1947, requesting assistance from the Chemical Division.

Rubout tests on current manufacture on the RT-364-DR process gave the following results versus the RT-364-D standard:

Lot 82336 vs lot 49274: lt., yellow - $\pm 10\%$ strong - yellow.

Shading with RT-431-D and blanc fixe gave the following results:

Mix vs lot 49274: vs dark and dull - s. blue - OK - vs. blue & dull.

As this was a far better match to the RT-364-D standard than could be obtained with K-2439 manufacture at the time it was decided to standardize on a dry mix process for RT-364-D. The low sales volume on this color and the probable difficulties connected with solving the K-2439 process problem helped to force this decision.

A new standard formula, RT-364-D(B), based on a dry mix of 78% RT-364-DR - 12% RT-431-D - 10% blanc fixe, was issued in February 1948. Cost analysis showed that an approximate 1-1/2 cents per pound saving in mill cost over the economy process, K-2439, results from the use of the dry mix procedure.

The plant assistance problem on RT-364-D was closed out in February, 1948, with the issuance of the dry mix process.

PATENT SITUATION:

There is no patent restriction in the manufacture of RT-364-D and RT-364-DR. It is not believed that this study has resulted in any patentable developments.

GLOSSARY:

RT-364-D - A barium lithol red toner (Tobias Acid $\rightarrow$ Beta Naphthol) containing approximately 12% Rosinated Calcium Lithol Red Toner and 10% Blanc Fixe.

RT-364-DR - A barium lithol red toner standardized for rubber.

RT-431-D - A rosinated calcium lithol red toner containing about 19% calcium rosinate.

Acid Coupling - Applied to lithol red coupling procedures in which an acid diazo is added to a very slightly acid precipitated beta naphthol slurry. There is no coupling reaction at this point. The mixture is then coupled to form the sodium salt of lithol red by the addition of a slight excess of caustic soda.

EXPERIMENTAL DETAILS:

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