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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

SEMI-WORKS DEVELOPMENT AND PLANT DEVELOPMENT AND STANDARDIZATION OF DIRECT LAKING PROCESS FOR RT-443-D.

Period Covered: March 1944 - January, 1948.

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: Semi-Works Development and Plant Development and Standardization of Direct Laking Process for RT-443-D.

Period Covered: March 1944 - January, 1948.

Charge: 1100-12-30 (AIC-30)

SUBMITTED BY: E. J. Hess E. J. Hess DATE SUBMITTED: June 7, 1948

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INTRODUCTION

Upon completion of laboratory study on the "Duol" Carmine toner direct laking formula, K-1994, (see KN-44-49) Semi-Works development work was started in March, 1944. Because of poor wetting and bad dusting characteristics of this color compared with the "isolated dye" RT-443-D standard, lot 32268, the process was returned to the laboratory for revision.

The dusting problem was solved in the laboratory by use of a treating agent, Resinous Oil X-1, (see KN-44-49) and the process returned to the Semi-Works for study in September, 1944. The results of this Semi-Works study are recorded in KN-44-69 and DSN-44-20.

Plant development and standardization work on the direct laking RT-443-D procedure was started in January, 1945, using the K-2039 process as the basis for the study.

SUMMARY & CONCLUSIONS

As is evident from the following discussion the Semi-Works and plant development study proved to be unusually complicated. The following brief outline covers the study chronologically.

K-1552 (Sept., 1941-) (Feb., 1942)

Original laboratory process. Increased batch size resulting from increased concentration and other factors indicated potential savings of about eleven cents per pound compared with the RT-443-D "isolated dye" formula, K-1587.

Disadvantages: poor wetting and dusting characteristics, high bulk.

Advantages: lower cost, improved texture.

Returned to the laboratory after short Semi-Works study (see KN-43-127 and DSN-43-51).

K-1994 (Jan., 1944-) (July, 1944)

First "all-lime" direct laking formula. The use of slaked lime (calcium hydrate) as a source of both calcium and alkali (replacing caustic soda and calcium chloride as used in K-1552) resulted in a saving of approximately one cent per pound. K-1994 type material, however, retained the poor wetting and dusting properties of K-1552 and after a short Semi-Works study (March, 1944) laboratory work was resumed to correct this disadvantage.

Laboratory work reported in KN-44-49. Semi-Works study is discussed below.

RT-443-D, K-2039

Modification of K-1994, using emulsified Resinous Oil X-1 as a treating agent to correct wetting and dusting properties. After a short Semi-Works development study the process was taken to the plant in January, 1945.

Laboratory work reported in KN-44-49. First Semi-Works study reported in KN-44-69 (DSN-44-20).

Subsequent Semi-Works and plant development studies are discussed below.

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RT-443-D, K-2237 — Poor quality of crude PTMSA (replaced purified material "Lithosol" acid RBA to realize calculated savings) made clarification of the sodium salt of the PTMSA necessary. This, in turn, because of sparing solubility of the calcium salt of PTMSA, motivated return to use of caustic soda instead of slaked lime in the PTMSA solution only; calcium chloride was added to the BON-slaked lime slurry to make up the calcium deficiency resulting from the change. Plant study was started in November, 1945. Laboratory and Semi-Works study reported in Memo report 1-28-46 (Semi-Works data filed in DSN-45-1). Plant work is discussed below.

RT-443-D, K-2489 (RT-443-D (A)) — Light masstone results with K-2237 made it necessary to revise the formula by adding a small amount of Tobias acid to the PTMSA as an "accessory" to increase masstone depth. A slight increase in blueness of tint also resulted. The RT-443-D direct laking standard, lot 80657, set up in July, 1947, is based on material of this type. Plant work using the Tobias acid variable was started in November, 1946, and is discussed below.

RT-443-D (B) — Continued difficulty with out-of-line light masstones and blue tints made it necessary to develop variables to obtain improved control. Return to the "all-lime" formula (K-2039 type), use of the Tobias acid "accessory" intermediate, careful control of coupling and development pH, and, finally, replacement of the K Wood with M Gum rosin corrected the difficulty. The standard direct laking process, RT-443-D (B), issued in December, 1947, was based on this work. The plant study of the "all-lime" formula was resumed in July, 1947, and is discussed below.

Testing Method — One of the principal problems resulting from the use of the direct laking process was the abnormally light masstone (compared with the "isolated dye" products) obtained with the bodied linseed oil vehicle (H-108) used for normal paint standardization at the time. Attempts to correct the difficulty by formula changes were unsuccessful. Tests made in the Paint laboratory, however, indicated that lithographic varnish, which did not give the objectionable light masstone characteristic, could be substituted for the bodied linseed oil. The revised testing method, TP-132-11, was issued in January, 1947.

The Production Division accepted supervision of the direct laking process for RT-443-D manufacture in January, 1948.

PATENT SITUATION

There is no patent restriction in the manufacture of direct laking "Duol" Carmine toner, RT-443-D. It is not believed that this study has resulted in any patentable developments.

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DISCUSSION OF EXPERIMENTAL STUDY

Three Semi-Works batches of RT-443-D were made during March, 1944, on the K-1994 procedure (the new "all-lime" direct laking formula for this "Duol" Carmine toner). "Lithosol" acid RBA, the pure standardized type of the PTMBA intermediate, was used in all cases. The principal differences between K-1994 and the original direct laking procedure, K-1552, follows:

1. Slaked lime is used as the source of alkali in both the PTMBA and BON solutions replacing caustic soda. The lime also is the source of the calcium precipitant replacing the calcium chloride added to the BON solution in the case of K-1552.

2. The sodium acetate buffer is omitted from the coupling.

3. The sodium rosinate amount is increased approximately 8%.

4. The BON volume for coupling is cut about 15%.

5. Coupling and development is accomplished at a slightly lower pH (pH 8.3 - 8.8 instead of pH 10.6 - 11.0).

Although the goal yield for K-1994 was on the low side (550#/mol as compared with 590#/mol for K-1552) a saving of one cent per pound for K-1994 compared with K-1552 was indicated.

The Semi-Works batches of K-1994 averaged vs dark and dull in masstone, 10% strong, and slightly yellow and intense in tint versus the "isolated dye" RT-443-D standard, lot 32268. Against the laboratory standard, K-1994, all of this production was dark and dull in masstone, equal in strength, and yellow in tint.

As this manufacture had the slow mixing, high dusting characteristics of K-1552 the process was returned to the laboratory for further study.

Laboratory work showed that a treatment with Resinous oil X-1 would correct the undesirable wetting and dusting characteristics of K-1994 and a new formula, K-2039, was written based on the results of this study.

K-2039 differed from K-1994 as follows:

1. The normal coupling and development pH was increased to 10.0 - 10.4 instead of 8.3 - 8.8.

2. About 33#/mol of Resinous oil X-1 (emulsified with a small amount of sodium rosinate) was added to the color slurry before heat development. About 60% of this material is retained in the pigment (equivalent to about 3% based on the weight of the color).

3. Coupling is accomplished at 95°F. instead of 104°F.

The K-2039 goal yield figure of 614#/mol represents a decided increase (11.%) over that for K-1994. The increased pH of coupling and development is probably mainly responsible for the yield improvement.

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A short Semi-Works study run during September - October, 1944 and reported in KN-44-69 (see DSN-44-20) showed that the process was workable and plant study was started in January, 1945.

Early plant manufacture (January - February, 1945) of direct laking RT-443-D was based on the K-2039 process using purified PTMSA ("Lithosol" acid RBA). Quality of the three batches made averaged slightly light in masstone, about 6% weak, and slightly blue in tint versus the "isolated dye" standard, lot 32268. Texture, mixing, and dusting characteristics were satisfactory.

All of the early cost and savings calculations on the direct laking RT-443-D process had been based on the use of a satisfactory crude PTMSA available at the time at a cost of about 50 cents per pound (the purified type, "Lithosol" acid RBA cost 80 cents per pound during the same period). Charges 438-451 of the crude material had been examined in the laboratory in early 1943 and had given satisfactory results.

Considerable difficulty was experienced in obtaining shipments of the crude material at the time because of the general shortage of all organic intermediates but finally a shipment was received (lots 3 and 17). Both of these lots were poor in quality (dark and dirty in appearance and contained a noticeable amount of black insoluble material) compared with the earlier receipts of crude material. Contact with the supplier, Orchem, indicated that an equipment change at the Chambers Works was probably responsible for the difficulty. It was stated that no improvement in quality of future shipments could be guaranteed and that duplication of the early samples of crude material received by the laboratory was very unlikely.

Five plant batches based on the K-2039 process using lots 3 and 17 of the crude PTMSA were made during June - July, 1945. Results checked the laboratory, all batches were dull in masstone.

Meanwhile, a laboratory and Semi-Works study designed to correct the difficulty was scheduled. Results indicated that filtration of the PTMSA solution prior to diazotization would decrease dullness of masstone to a noticeable extent. At the same time it was recommended that caustic soda instead of slaked lime be used for dissolving the PTMSA because of the greater solubility of the sodium salt which decreased the probability of intermediate loss during clarification (see Memo report 1-28-46; DSN-45-1).

Five plant batches were made during the latter part of 1945 using the PTMSA solution clarification revision. Results indicated that the new variable would not completely solve the dull masstone problem but a definite improvement was obtained. A new shipment of "crude" material used in three of these batches, lot 83, was found later to be purified PTMSA shipped as crude to complete an order. Masstone control in this series remained unsatisfactory and varied over a wide range in depth. Average masstone quality was fairly good (slightly light versus the standard, lot 32268).

A new formula, K-2237, based on the revised process was set up in July, 1946, as the first direct laking standard formula for RT-443-D. K-2237 differs from the previous direct laking procedure, K-2039, as follows -

1. The batch size is increased to 1.47 mols from 1. mol.

2. Caustic soda is substituted for slaked lime as the alkaline solvent for the PTMSA. The resulting calcium deficiency is adjusted by adding calcium chloride to the BON slurry.

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3. Crude PTMSA is substituted for the "Lithosol" acid RBA.

4. The alkaline solution of PTMSA is treated with Filtercel and activated carbon black and clarified prior to diazotization.

5. The diazo volume is increased by about 33%.

6. Drying temperature is definitely set at 160°F. Laboratory drying at 140°F was satisfactory but the use of this temperature in the Semi-Works and plant resulted in under-drying (light-weak-yellow products).

Meanwhile, a number of contacts were made with Orchem in an attempt to improve the crude PTMSA quality situation. An attempt was made by Newark to set up charge 9 as a standard but Orchem would not agree to this because of its comparatively good quality (letter A.S. to C.K.D., 7/27/45). Finally, lot 4 (charge 35), which was of slightly poorer quality, was set up as a compromise standard by Orchem and Newark (letter A.S. to K.O.J. 2/18/46). Neither of these lots was equal in quality to the original laboratory trial samples which were practically equal to the purified material.

An attempt to set up a plant direct laking type standard for RT-443-D was unsuccessful. The proposed standard, lot 46884, a blend of four batches made on the K-2237 formula during the latter part of 1945, was rejected because of unsatisfactory bleed in lacquer over-stripe (probably a result of contamination). In color, lot 46884 was a close match to the "isolated dye" standard, lot 32268, by varnish drier rubout but in H-108 vehicle (bodied linseed oil) the masstone was light. This light masstone effect in the H-108 vehicle presented a problem of considerably importance in the development of direct laking RT-443-D as a major proportion of this color is standardized for paint use and the H-108 rubout was the official paint standardization test at the time. Investigation of the vehicle variation was carried on in conjunction with the formula study.

Manufacture on the K-2237 process was continued during July and August, 1946. Nine batches were made. All of this production averaged light, slightly dull in masstone and slightly blue and dull in tint in H-108 vehicle. In varnish dryer, masstones averaged close to the standard, lot 32268. An undesirable characteristic of these batches was weakness of tint. In testing these batches it was noted that long rubout series (7 or 8 samples) rubbed on the Hoover muller gave poor duplication of masstone results and a definite tendency toward light masstones. Heating up of the muller with prolonged use was indicated as a possible reason for this masstone change and hand-mulling was used in all subsequent work.

Because of the continued production of light masstone material it was decided to introduce small amounts (up to 10 pounds per 1.47 mol batch) of Tobias acid ("Lithosol" acid TOB) into the PTMSA diazo to increase depth of masstone. This material had been successfully used in the laboratory as a dark masstone variable. The slight increase in blueness of tint resulting from adding the Tobias acid was acceptable to Sales.

Production on the modified K-2237 formula continued intermittently from November, 1946, to July, 1947. Forty seven batches were made during this period. Variables tried and the results obtained follow:

1. Variation in Tobias acid from none to ten pounds per 1.47 mol batch gave the expected results. Batches without the "accessory" were light in masstone by

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both H-108 oil and varnish dryer rubout, about 5% weak and slightly blue in tint versus the standard, lot 32268. Ten pound additions gave dark, dull masstones in both vehicles, and blue and dull tints. Results indicated that the use of four pounds of Tobias acid would given a fairly close approximation to standard depth in varnish drier (light in H-108 oil) and somewhat bluer tint. Non-duplicability of the formula, particularly in masstone and tinting strength (considerable tendency toward production of light masstone and weak tints), made close control of masstone difficult even with the use of the Tobias acid variable.

2. Results showed that close control of coupling and development pH was necessary for satisfactory strength. Control of coupling pH by pH adjustment of the PTMBA before diazotization and of the BON slurry before adding the sodium rosinate gave only fair control. Best strength results in this series were obtained under the following conditions:

   a. pH of the PTMBA + Tobias acid before diazotization: 10.0 - 10.5; adjusted with caustic soda or hydrochloric acid before clarification.

   b. pH of the BON - lime slurry: 10.3 - 10.7; adjusted with caustic soda or hydrochloric acid before addition of the sodium rosinate.

   c. Coupling pH: 7.0 - 9.0; not adjusted. Couplings in the pH 10.0 - 11.0 range ground out weak in tint.

   d. Development pH: 9.8 - 10.2; adjusted before addition of the Resinous oil X-1 with caustic soda or hydrochloric acid. Adjustment of pH before development can be used to control quality contrary to original laboratory reports.

Masstone control was poor even with satisfactory strength performance. Many of the batches were light with normal amounts of Tobias acid (3-4 pounds). Dark masstone products were only obtained by the use of increased amounts of the accessory (8-10 pounds) which also gives increased dullness of masstone and blueness and dullness of tint.

3. Omission of the Resinous oil X-1 gave an approximate 10% increase in strength and an improvement in texture at the expense of poor wetting characteristics. A reduced amount (25 pounds instead of 49 pounds in the 1.47 mol batch) seemed to give a slight strength improvement without affecting wetting to any extent.

4. A Semi-Works study (6 batches made during January, 1947) indicated that better masstone and strength control could be obtained if the calcium chloride was added to the PTMBA solution after clarification instead of to the BON-lime slurry. The amount also was increased (147 pounds instead of 104 pounds per 1.47 mol batch) to more closely approach the excess of calcium salt present in the K-2039 all-lime process. Subsequent plant experience indicated that a slight advantage resulted and this change was introduced into the plant K-2237 procedure.

The above vehicle change made it possible to select from current manufacture the components of a blend that would give a reasonably close match to the "isolated dye" RT-443-D standard, lot 32268. Accordingly, a mix of six plant batches made during February and March, 1947, lot 80657, was set up as the RT-443-D direct laking standard in July, 1947.

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A rubout comparison of the new versus the old standard follows:

Lot 80657 vs lot 32268: vs light - vvs blue - OK - s blue
toluene bleed: vs worse.

A formula based on the process used for the standardization material was issued in June, 1947, as standard RT-443-D, K-2489. This process was subsequently designated RT-443-D (A). K-2489 differed from the previous process, K-2237, as follows:

1. Approximately 0.9 mol % Tobias acid (3 pounds per 1.47 mol batch) was substituted for part of the PTMSA in the diaso. This increases masstone depth at the expense of a slightly duller masstone and slightly bluer and duller tint.

2. The pH of the PTMSA - Tobias acid solution before clarification was decreased from 10.0 - 11.0 to 10.0 - 10.5. This change was made to lower coupling pH and to obtain more consistently satisfactory masstone and strength.

3. The calcium chloride was added to the PTMSA solution instead of to the BON slurry. The weight was increased from 104 to 147 pounds. Both of these changes gave a closer approximation to the original K-2039 (all-lime) process and seemed to give slightly better quality control.

4. The BON slurry was adjusted to a pH of 10.3 - 10.7 instead of 10.8 - 11.0 before coupling. This change was also a factor in controlling coupling pH to obtain improved quality performance.

5. The coupling was adjusted to a pH of 9.8 - 10.2 instead of 10.0 - 10.4 before adding the resinous oil emulsion and heat development.

6. The resinous oil amount was decreased from 49 to 25 pounds.

Even following the change of standard pigment, performance with the K-2489 process was poor; most of the batches ground out on the light side. Increasing the Tobias acid gave darker masstone but tints were too blue and dull. This necessitated further development work in the plant and Semi-Works to correct the difficulty.

Finally, it was decided to return to the K-2039 (all-lime) formula as a basis for plant production in order to secure better quality control, that is, darker masstone and yellower tint.

Plant production using a modified K-2039 procedure was started in July, 1947. Forty-eight batches were made during the period July, 1947 to January, 1948. Early masstone performance was only slightly better than that obtained with the K-2489 process but, gradually, the quality was brought under control. During the course of the work the following variables were studied:

1. Variations in the Tobias acid ranging from omission to addition of 5 pounds per batch. The use of 4 pounds seemed to give the most consistent match for standard.

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2. Results indicated that better control was established if the Tobias Acid was added to the lime solution of PTMSA after clarification. Two pH adjustments of the PTMSA solution, one before filtration (to obtain good solubility and cut down loss of PTMSA in the press) and one after the Tobias acid (to obtain optimum coupling pH) were made necessary by this change. Recommended for the initial adjustment is a pH of 9.0 - 9.5 and for the final a pH of 9.5 - 10.5.

3. As plant production continued out of line on the light side a Semi-Works series of nine batches were made during September - October, 1947, in an attempt to develop a dark maastone variable with a minimum tint effect. All of the Semi-Works experimental batches ground out darker and stronger than the standard, lot 80657, even when the Tobias acid was omitted. It was also noted that batches made without clarification using purified PTMSA were darker than usual in maastone. It was concluded from this that rapid processing of the PTMSA solution (measuring from the stirring together of the PTMSA and the slaked lime to the addition of the acid for diazotization (this included the time for clarification) gave maximum depth and strength. Accordingly, the plant operation was re-arranged to reduce the stirring time of the PTMSA-lime solution to a minimum. By scheduling the making of the BON-lime slurry and clean-up of the clarification press before addition of the PTMSA to the slaked lime it was found possible to cut the over-all stirring time of the PTMSA solution from about four hours to about two hours. In the Semi-Works, the same operation takes one hour. Although no appreciable improvement in maastone depth or in tinting strength was noted in the plant the change was retained as potentially establishing a more controllable process.

4. Separate diazotization and addition of the Tobias acid diazo showed no advantage in the Semi-Works or plant.

5. Substitution of M Gum for K Wood rosin gave a decided improvement in maastone-tint relationship. With the M Gum rosin it was found possible by a proper combination of variables to obtain dark, yellow shading material. A product of this type was almost impossible to manufacture when using K Wood rosin.

The present standard formula, RT-443-D (B), based on the information developed during this period, was issued in December, 1947. RT-443-D (B) differs from the "A" formula (K2489) as follows:

1. The formula is set up on a step wise basis.

2. Slaked lime is substituted for caustic soda for use in dissolving the PTMSA. The calcium chloride added to the PTMSA in the "A" formula is omitted.

3. The Tobias acid accessory amount is increased to 1.2 mol% (4 pounds instead of 3 pounds). The Tobias acid is added after the PTMSA solution clarification.

4. The PTMSA solution pH before clarification is lowered to 9.0 - 9.5 to decrease the "salting-out" effect noted in higher alkali concentrations.

5. For better control of coupling the PTMSA-Tobias acid solution is adjusted after clarification to a pH of 9.5 - 10.5.

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6. The over-all stirring time of the PTMSA solution before diazotization is held to a maximum of 2-1/2 hours for better quality control.

7. The diazo volume is cut by approximately 25%.

8. The pH of the BON slurry before coupling is increased to 10.8 - 11.0.

9. M Gum rosin is substituted for K Wood rosin.

10. The pH for development is increased to 10.0 - 10.4.

Following is a tabulation of the plant yield performance and the approximate savings possible with each direct laking process compared with "isolated dye" formula, K-1587:

Formula	Number of Plant Batches	% of Goal Yield (834# per 1.47 mol)	approximate savings in mill cost per 100# compared with K-1587.
K-1552 (1 mol)	-	-	$11.00
K-2039 (1 mol)	8	98.5%	16.00
K-2237 } RT-443-D (A) }	61	99.4%	20.00
RT-443-D (B)	48	102.6%	20.00

The Production Division accepted supervision of the direct laking process for RT-443-D manufacture in January, 1948.

GLOSSARY

RT-443-D The rosinated calcium salt of the coupling of PTMSA diazo and Beta hydroxy naphthoic acid. About 26.% of calcium rosinate is present in the finished toner.

PTMSA Para toluidine meta sulfonic acid.

"Lithosol" Acid RBA Purified PTMSA.

BON Beta hydroxy naphthoic acid.

Tobias Acid Beta naphthylamine- 1 sulfonic acid.

Resinous oil X-1 An oily product of 100% coal tar origin. It has no acid number. Flash point 250°F. min.
Supplier: Neville Company, Pittsburg.

Slaked lime Calcium hydroxide - chemical grade
Minimum CaO 70.0%.

Direct Laking Preparation of the finished pigment from the basic intermediates without isolation or removal of the mother liquor from the dyestuff.

EXPERIMENTAL DETAILS RT-443-D Semi-Works DSN-48-4.
RT-443-D Plant DSN-48-5 Parts I-II-III-IV.

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