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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

SEMI-WORKS DEVELOPMENT AND PLANT DEVELOPMENT AND STANDARDIZATION OF DIRECT LAKING PROCESS FOR RE-526-D.

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

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SEMI-WORKS DEVELOPMENT AND PLANT DEVELOPMENT AND STANDARDIZATION OF DIRECT LAKING PROCESS FOR RE-526-D.

FEBRUARY, 1945 - APRIL, 1948.

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INTRODUCTION:

The plant development of the direct laking procedure for RE-526-D (extension of a dark masstone RT-443-D type toner (23%) on Barytes) was started in February, 1945. A short laboratory study had been completed (See KN-44-49) and this, together with available semi-works and plant information on the direct laking procedures for RT-443-D (see KN-48-8), was used in selecting the starting formula.

SUMMARY & CONCLUSIONS:

As is evident from the following discussion, the plant development study proved to be unusually complicated.

As in the case of RT-443-D, the following factors were important in the final solution of the problem:

1. Use of Tobias Acid as an "accessory" intermediate.
2. Control of coupling and development pH.
3. Use of M Gum rosin.
4. Substitution of lithographic varnish (varnish dryer) for bodied linseed oil (H-108 vehicle) as the testing vehicle.

A standard process for direct laking "Duol" Carmine Lake, RE-526-D(B), was issued in April, 1948. The RE-526-D standard, lot 84614, based on this process was set up in March, 1948.

The Production Division accepted supervision of the direct laking process for RE-526-D manufacture in April, 1948.

PATENT SITUATION:

There is no patent restriction in the manufacture of direct laking "Duol" Carmine Lake (RE-526-D). It is not believed that this study has resulted in any patentable developments.

DISCUSSION OF EXPERIMENTAL STUDY:

As the K-2039 toner formula (modified K-1994 using a resinous oil treatment) had already supplanted K-1994, this "all-lime" formula was used in the first plant batch. The original laboratory procedure for the extended product, K-2013, was based on K-1994. The first batch ground out slightly light and dull in masstone, close in strength, and slightly yellow and clean in tint versus the "isolated dye" RE-526-D standard, lot 4290.

A second batch made in June, 1945, using crude PTMSA instead of the purified type ("Lithosol" Acid RBA) was darker and duller in masstone and slightly bluer in tint than standard.

Both of these batches were vat washed; this may account for the low yields obtained (grind yields averaged about 85% of goal).

Meanwhile, because of its low selling price, RE-526-D was showing a paper loss of about 10%. In order to correct this the Sales Division recommended that the toner content of this color be cut to 20.8% from 23.1%. On the basis of this, a direct laking RE-526-D standard formula, K-2268, was written to replace the "isolated dye" procedure, K-1891. The K-2268 process was based on the RT-443-D toner formula, K-2237, and differed from the original RE-526-D laboratory procedure, K-2013, as follows:

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

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

3. Crude PTMSA was substituted for the purified material, "Lithosol" and RBA.

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

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

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

7. Coupling was accomplished at 95°F instead of 104°F.

8. About 33#/mol of Resinous oil K-1, emulsified with sodium rosinate, was added to the color slurry before heat development.

Production on the K-2268 formula was started in July, 1946. Two light masstone, 20% weak tint batches were made. After discussing these results with Sales it was decided to return to the original 23.1% toner content for this color. This necessitated a decrease of 13% in the amount of barytes extender used.

Manufacture was continued on the modified K-2268 procedure. Fifteen batches were made during the period August, 1946 to June, 1947. Almost all of this production was light in masstone versus the "isolated dye" standard, lot 4290, by the standard testing method, TF-95-12((a bodied linseed oil (H-108 vehicle) rubout)). The use of the H-108 vehicle was principally responsible for the light masstone and presented a problem similar to that experienced with the standardization of the direct laking process for RT-443-D (see KN-48-8). However, the solution of the RT-443-D problem (January, 1947) by the substitution of the varnish dryer vehicle for H-108 was not the answer in the case of RE-526-D as the standard testing method for the extended pigment was supplied by the principal customer, Sloan-Blabon, and could not be revised without further study.

During this period a number of variables were tried in an attempt to improve masstone and strength control. The variables tried and the results obtained follow:

1. In line with experience on the RT-443-D toner, Tobias Acid was used as an accessory diazo intermediate in RE-526-D to obtain dark masstone. About six pounds per 1.47 mol batch gave the maximum acceptable increase in blueness of tint but masstone remained light in the H-108 vehicle. In varnish dryer, results were fairly close to the desired depth. RE-526-D masstone standardization is complicated by the fact that the original standard, lot 4290, was set up out of line dark in masstone in order to meet customer requirements.

2. Close control of coupling and development pH was found to be necessary for optimum depth of masstone and strength and yellowness of tint. Fairly satisfactory strength was obtained by adjusting the PTMSA-Tobias Acid solution pH to 10.0-10.5 (before diazotization) and the BON-lime slurry to a pH of 10.3-10.7. This gave a coupling pH in the range of 7.0-9.0 which on adjusting to a pH of 9.8-10.4 before heat development gave fairly satisfactory toner strength. However, masstones by H-108 subout were still on the light side of standard and varnish dryer rubouts were inconsistent.

3. Doubling the standard amount of Resinous oil (99# instead of 49#) gave a definitely weaker and somewhat lighter and bluer product. Decreasing the resinous oil to 25 pounds had little, if any, tinctorial effect.

4. Addition of the calcium chloride precipitant to the diazo in the manner of the RT-443-D toner formula, K-2489, gave improved quality control and was used in most of this production.

5. Early in the work it was discovered that the theoretical amount of extender (2950# or 76.9% based on a toner goal yield of 896#) was giving strength results in the order of 10-15% weaker than standard. Decreasing the extender to 2500 pounds gave products about 5-10% stronger than standard. Subsequently, a goal yield re-check indicated that the standard extender amount should be 2745 pounds (76.9% based on a toner yield of 834#).

A short semi-works study run during September-October, 1946, in an attempt to develop a dark masstone variable was the basis for the introduction of Tobias Acid as an "accessory" intermediate. Tobias Acid substituted for PTMSA to the extent of 3 mol % gave a product close in depth and blue in tint versus the RE-526-D standard, lot 4290. The use of PTOSA and OTMSA as a replacement for the Tobias Acid in the same molar amount gave lighter, weaker and yellower products. The information which indicated the desirability of adding the calcium chloride to the diazo instead of to the BON-lime slurry was also developed in the semi-works at this time.

Almost from the start of the plant development work complaints were received from the Control Division that the oil absorption seemed to be definitely lower than the standard. One of the customers (Armstrong), by specification, permits only a 5% variation from standard in this characteristic for normal shipments. Examination of a number of batches during March-April, 1947 indicated a range of oil absorption variation from 7% to 29% on the low side. Oil absorption measurements of the toner components of these batches varied from 95% on the low side to 107% on the high side of the"isolated dye" RT-443-D toner standard, lot 32268. The direct laking process, therefore, does not seem to be responsible for the low oil absorption. Subsequently, it was discovered that the barytes extender in use at the time showed a definitely lower oil absorption than the standard barytes sample. Later shipments of barytes appeared to be more normal and no difficulty was reported.

When poor quality performance on the RT-443-D toner made it desirable to return to the "all-lime" formula (K-2039 type) the RE-526-D toner process was changed accordingly.

Plant production of RE-526-D based on the "all-lime" formula was started in July, 1947. Twenty-six batches were made during the period July, 1947 to April, 1948. Toner quality performance(by varnish dryer rubout) showed a definite improvement but H-108 results on the extended material were still on the light side of standard.

During this period (September, 1947) a second semi-works study was made using the "all-lime" formula as a basic procedure in an attempt to develop a variable to give dark masstone with the H-108 vehicle. Although all of the semi-works manufacture was darker and stronger than comparative plant production, no definite improvement was obtained by -

1. Separate diazotization and coupling of the Tobias Acid.

2. Separate diazotization and coupling of PTOSA substituted for the Tobias Acid (this gave light masstone).

3. A 30% increase in coupling volume.

Plant variables and the results obtained using the K-2039 type (all-lime) toner formula follows:

1. Variation in Tobias Acid in the range of 4 to 6 pounds gave light masstones and blue tints versus standard in the H-108 vehicle. In varnish dryer, 5.7 pounds of Tobias Acid gave a fairly close match to the desired depth of masstone and hue of tint.

2. Results indicated that better quality control was established (better pH control) if the Tobias Acid was added to the PTMSA-lime solution after clarification. Two pH adjustments of the PTMSA solution prior to diazotization are used under these conditions. Recommended for the initial adjustment before clarification is a pH of 9.0-9.5 and for the final adjustment after the addition of the Tobias Acid a pH of 9.5-10.5.

3. As described in the RT-443-D report (KN-48-8) rapid processing of the PTMSA-lime solution in the semi-works gave improved depth and strength. Although no marked improvement resulted in the plant the change was retained as potentially establishing a more controllable process. However, results indicate that where PTMSA quality permits elimination of the clarification step a definite increase in masstone depth is obtained.

4. Separate diazotization and coupling of the Tobias Acid showed no advantage in the plant (checking semi-works results).

5. Substitution of M Gum for K Wood rosin gave a definite increase in depth of masstone with little or no change in tint.

6. Use of the 834# goal yield for the toner gave satisfactory RE-526-D strength at the 23.1% toner level. The standard extender amount for the 1.47 mol batch is 2745 pounds.

Failure to develop a variable that would give the desired depth of masstone in the H-108 (bodied linseed oil) vehicle made it necessary to consider the possibility of using varnish dryer standardization. After a number of tests were made using RE-526-D alone and in combination with YE-421-D (Molybdate Orange) Sales finally decided to permit standardization of the direct laking material using "varnish dryer" to replace the H-108 vehicle.

A blend of five batches (made during the period October to December, 1947) lot 84614, was proposed as the first direct laking standard for RE-526-D and was set up in March, 1948.

Comparisons of the new versus the old standard follows:

Varnish dryer rubout (TF-132-11)
Lot 84614 vs lot 4290: vs dark-trace blue-OK-blue

H-108 rubout (Sloan-Blabon rubout) (TF-95-12)
Lot 84614 vs lot 4290: light-vvs strong-blue

Oil Absorption: Lot 84614: 15.2%; Lot 4290: 16.0%

Linoleum Composition:
Lot 84614 vs lot 4290: vvs blue, vs intense-5% weak-vs blue.

A formula based on the process used for the standardization material was issued in April, 1948, as standard RE-526-D(B). The "B" formula differs from the "A" process (formerly designated K-2268) as follows:

1. Hydrated lime is substituted for caustic soda for dissolving the PTMSA. The calcium chloride added to the BON slurry in the "A" formula is omitted.

2. Approximately 1.5 mol% of Tobias Acid is sibstituted for PTMSA in the diazo to obtain the desired masstone depth. A bluer tint also results. The Tobias Acid is added after the PTMSA solution clarification.

3. The PTMSA solution pH before clarification is maintained at pH 9.0-9.5 to decrease the "salting out" effect noted at higher alkali concentration.

4. As the addition of the Tobias Acid lowers the pH in varying amounts, the PTMSA-Tobias Acid solution is adjusted after clarification to a pH of 9.5-10.5 to maintain control of coupling.

5. 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.

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

7. M Gum rosin is substituted for K-wood rosin.

8. The Resinous Oil X-1 amount is cut by approximately 50%.

9. The Barytes extender amount is cut by 18% to return to the original standard toner content.

Following is a tabulation of the plant yield performance and the approximate savings possible with each direct laking process compared with the "isolated dye" formula, K-1891:

Formula	Number of Plant Batches	% of Coal Yield ("A" 423# per 1.47 mol) ("B" 356# " 1.47 mol)	Approximate Mill Cost Savings per 100# compared with K-1891
RE-526-D(A) (K-2268)	2	93.7%	$3.50
RE-526-D(B)	20	98.0%	0.50

The Production Division accepted supervision of the direct laking process for RE-526-D manufacture in April, 1948.

GLOSSARY:

RE-526-D - A 23.1% extension of dark masstone RT-443-D on barytes.

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.

PTOSA - Para Toluidine Ortho Sulfonic Acid.

PTMSA - Para Toluidine Meta Sulfonic Acid.

OTMSA - Ortho 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 Co., Pittsburgh.

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:

RE-526-D Semi Works DSN-48-6

RE-526-D Plant DSN-48-7 Parts 1 and 2