Serial No. KN-44-52

Copy No. /

E. I. DU PONT DE NEMOURS & COMPANY
KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

KN-44-52.

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Progress Report

PLANT AAND SEMI WORKS PRODUCTION OF "LITHOSOL" SCARLET 2YLN DYE, TONER AND LAKE, BF-4, RT-488-D AND RM-473-D.

Period Covered: October 1941 - January 1944

FILE: 222.25

DATE: 9-11-44

222.25

NJ8638

Serial No. KN-44-52

Copy No. 1

Copy to:

#1 - Numerical File
2 - Research Office (222.25)
3 - Library File (222.25)
4 - #10 Building File
5 - # 6 " "
6 - Imperial Chemical Industries, Ltd.
7 - " " " "
8 - " " " "
9 - Mr. C. H. Rupprecht, Wilmington (ICI File) Rec'd by Library 4-10-45

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

Title: PLANT AND SEMI WORKS PRODUCTION OF "LITHOSOL" SCARLET 2YLN DYE, TONER AND LAKE, SF-4, RT-488-D AND RM-473-D.

Period Covered: October 1941 - January 1944

SUBMITTED BY: E. J. Hess E. J. Hess DATE SUBMITTED: 8-4-44

APPROVED BY: V. Chalupski V. Chalupski Sept. 7, 1944 DATE ISSUED: 9-11-44

INTRODUCTION:

Production of both RT-488-D and RM-473-D has been active at intervals over the past two and one-half years.

Because of difficulty with the process it has been necessary to manufacture a good portion of the RT-488- D in the Semi-Works.

The substandard stock situation on RT-488- D has been helped to a considerable degree by the fact that all of the RM-473-D production has been of the "Muench-mixed" type. It has been possible to consume most of the difficultly shadeable weak RT-488-D substandard in this color (this, of course, increases production cost on RM-473-D to some extent).

Production of the Scarlet 2YLN dye, SF-4, has also been active in the Semi-Works and plant. A new plant procedure (based on a slight revision of a laboratory formula, K-1522) for the dye, K-1971, has been set up to replace K-1021. A considerable amount of RT-488-D has also been made from available Dye Works manufacture of 2YL dye.

Results on the following production are discussed in this report:

RT-488-D, Semi-Works manufacture	119 batches
RT-488-D, Plant manufacture	45 batches
RM-473-D, Muench mixed in the plant	18 mixes
SF-4 , 2YLN dye, Semi-Works manufacture	15 batches
SF-4, 2YLN dye, Plant manufacture	14 batches

SUMMARY AND CONCLUSIONS:

SF-4, 2YLN Dye - Semi-Works Production

Nine of the fifteen Semi-Works batches of 2YLN dye were based on the K-1021 formula or slight modifications thereof.

In general, RT-488-D toners made from these batches were shadeable although there was a noticeable amount of fluctuation from batch to batch particularly in masstones and tints. It is probable that most of the quality inconsistency in the toner was due to the poor duplicability results secured with the toner formula rather than to any deficiency in the intermediates or the dyestuff.

A number of variations in the standard K-1021 formula designed to give improvements in quality or in ease of manufacture were tried. A discussion of results follows:

1. Coupling on the surface, which would give more flexible plant operation, was tried. No quality disadvantage resulted and the revised procedure may be used in the plant when necessary.

2. The use of the dyestuff in press cake form rather than as the dried lump gave a useable product in the Semi-Works. Subsequent experience in the plant indicated that if the dye is retained in pulp form for too long a period (one month or more) partial deterioration occurs which results in the production of light, weak toners.

Because of the erratic performance of Scarlet 2YLN toner production the laboratory was requested to run variable studies on both the dye and the RT-488-D formulas in an attempt to develop more duplicable formulas. or an efficient set of control variables. As a result of this study (reported in KN-42-37) the K-1522 dye formula was developed which differs from K-1021, principally, as follows:

1. The total soda ash amount in the dye coupling is increased by 50% over the K-1021 figure.

2. Coupling is accomplished at 75°F instead of 35°F.

3. K-1522 is heat developed at 104°F as compared with the boiling development of K-1021.

Semi-Works experience with the K-1522 formula (6 batches made) indicated that:

1. There was some advantage in the quality of the RT-488-D obtained with the new dye (darker and yellower toners were secured).

2. K-1522 dye was considerably easier to filter because of the thin consistency of the slurry as compared with the heavy, foamy slurry obtained with the K-1021. Pressing losses are probably lowered with the more filterable material.

3. The dye may be used in press cake form but the wet cake deteriorates with age in a manner similar to the K-1021 type.

4. On drying the K-1522 type dye a hard, dense lump is obtained which must be ground before use in RT-488-D manufacture. This differs from the soft, bulky lump secured with K-1021 which wets readily and requires no grinding.

Because of the need for a satisfactory control variable for the production of dark, yellow RT-488-D it was decided that all subsequent plant production of 2YLN dye should be based on K-1522.

SF-4. 2YLN dye - Plant Production

Eight of the fourteen plant batches of Scarlet 2YLN were based on the K-1021 formula. In all of these batches a 12 1/2% increase in the caustic soda used for dissolving the 2YLN base (para-chlor aniline ortho sulfonic acid) was used in order to insure complete solution of the intermediate.

A description of the changes made in this modified K-1021 formula and the results obtained follow:

1. Two batches made on the modified formula using the K-1021 batch size (423# dry) and following the normal plant manipulation (coupled in Vat 310 and pumped to Vat 208 for the heat development) gave normal light, yellow shading RT-488-D toners.

2. Three double size batches (846# dry) were made on the above basic formula using Vat 200 for coupling and development. These batches were held in pulp form at the start but were finally dried out (after standing about two weeks). Raw material tests indicated that the dyes were satisfactory in both pulp and dry form and subsequent experience in Semi-Works and plant production was also normal (light, blue and light, yellow products of "OK strength" were obtained.

3. In order to prepare a dye that would give dark, strong blue toners a dye batch was made on the above double size formula except for the substitution of 3 mol % of Para toluidine ortho sulfonic acid for the regular 2YLN base. PTOSA has found considerable use in Red 2B as an accessory intermediate and had given the desired dark, blue type 2YLN dye in laboratory and Semi-Works trials. This dye lot was held in pulp form and a laboratory test immediately after preparation showed that the desired dark masstone, "OK strength", blue tint toner could be secured with this material. Approximately two weeks from the date of this test two plant batches of RT-488-D toner were made from the paste dye and unsatisfactory weak products were obtained. A second test of the paste dye was then run in the laboratory and a dark, very weak, blue product resulted. The paste dye was immediately dried out but subsequent experience in the Semi-Works showed that the dye had deteriorated to such an extent as to make it almost useless for RT-488-D production.

4. Two batches were made on the double size (846#) formula using Vat 207 to couple (this vat is 15% smaller than Vat 200) and drying out the paste dye immediately after filtration. Because of the considerable foam produced during heat development it was impossible to develop at the boil, temperatures in the order of 200°F. were obtained. Quality was fairly satisfactory except for difficulty in obtaining dark masstone. Tints were uniformly blue when normal variables were used.

Because of the considerable amount of light, blue RT-488-D toner substandard being built up with the modified K-1021 type dye, it was decided to use a new laboratory procedure, K-1522, in subsequent plant dye manufacture. K-1522 had been used successfully in the Semi-Works to secure dark, yellow shading material.

In December 1942, two plant batches (860# each) of K-1522 type dye were made. Although plant toner production did not respond to the variables ordinarily used for producing dark, yellow material in the Semi-Works a number of easily shadeable dark, slightly strong,

blue batches were made. No particular difficulty was encountered in making either dark, yellow or dark blue toner in the Semi-Works. at this time.

Nothing more was done on dye manufacture until October 1943, when four more plant batches were made using the K-1522 procedure (a plant formula for this process had been set up and coded SF-4, K-1971). Toner production in the Semi-Works and plant from these four dye lots has been somewhat inconsistent in quality but the majority of the batches made have been definitely weaker than standard. No reason can be advanced at present for the apparently poor quality of this dye.

Following is a tabulation of the average yields obtained with the K-1021 and K-1522 type formula in the plant and Semi-Works:

	K-1020	K-1522
Number of SW batches	9	5
% yield (416# N-463 = 860# dry dye)	98.4%	105.0%
Number of Plt. batches	7	5
% yield (416# N-463 = 860# dry dye)	101.1%	109.7%

Actual dye content of the dry dye is in the order of 85-87%.

RT-488-D Toner - Semi-Works Production

A new standard formula, K-1436, was used in this Semi-Works RT-488-D production. K-1436 differs from the old laboratory formula, K-9669, as follows:

1. The batch size is cut from .5 mol to .345 mol.

2. The dye is used "as is " 100% instead of the K-9669 figure of 96% (Dyeworks dye). This has the nominal effect of increasing all the other ingredients (sodium rosinate and calcium chloride) as well as the strike volume by 4%. It may be mentioned that for our own 2YLN manufacture a figure of 86% for the dye content of the dry dye would be closer to the fact.

3. The dye volume before adding the rosinate is cut from 4800 gallons at 105°F. to 4260 gallons at 85°F. This represents an 11% volume cut.

4. The strike temperature is reduced from 105°F. to 90°F.

5. The struck slurry is heat developed at 145°F. for 30 minutes instead of at 155°F. for 10 minutes.

Semi-Works production for the period October 1941 to January 1944 may be divided into the following three general categories:

1. Manufacture to supplement plant production (prepare dark, yellow shading material difficult to obtain in the plant).

2. Development of new control variables.

3. Testing of plant and Semi-Works dye.

A number of variable combinations were tried in the course of this work. The modifications used and the results obtained follow:

1. Modified K-1436: Batch Size: .05-.1 mol
Sodium rosinate: 25-35% increase
Calcium chloride: 5-10% increase
Development temp.: 140-155°F.

Of thirteen batches made in this manner seven were of the expected dark, ok, blue type; two were dark in masstone, equal in strength and clean in tint and one was dark, ok, and yellow. The remaining three batches were blue in tint but very weak. No great amount of the weak product can be consumed in RT-488-D mixes but it can be readily used, at a cost, in the Muench-mixed extended product, RM-473-D.

2. Modified K-1436: Batch Size: .1-.2 mol
Sodium rosinate: 25-35% increase
Calcium chloride: 5-10% increase
Development temp.: 160-175°F.

This combination of variables was used in an attempt to obtain material close to standard. Various types of dye, including Dye Works 2YL and plant and semi-works manufacture of 2YLN, were used. Tinctorial results on nine batches were quite inconsistent except for strength which remained fairly close to standard. No definite trend towards any particular type product was noted as the following masstone-tint combinations were obtained: dark-blue, dark-yellow, light-blue, and light-yellow.

3. Modified K-1436: Batch Size: .1-.3 mol
Sodium rosinate: 40-60% increase
Calcium chloride: 5-10% increase
Development temp.: 155-170°F.

Results on eleven batches using the above combination of variables showed a slight trend towards the production of light-very slightly weak-blue material (five of the batches were of this type). Three of the remaining six batches were dark and blue, one dark in masstone and clean in tint, one light and yellow and one dark and yellow versus the RT-488-D standard. Only one of these batches was definitely weak and in this case the use of an "off" lot of dye was believed to be responsible.

4. Modified K-1436: Batch Size: .1 mol.
Sodium rosinate: 60% increase
Calcium chloride: 6% increase
Development temp.: boil

A single batch using the above variables ground out light, weak and very blue versus standard. This effect is in line with previous experience.

5. Modified K-1436: Batch Size: .05-.1 mol.
Sodium rosinate: 25-35% increase
Calcium chloride: 5 to 30% decrease
Development temp.: 140-155°F.

The use of the lowered precipitant excess variable is based upon laboratory work which indicated that some of the difficulties with extreme weakness of tint could be eliminated by this method. Most of these batches were made with approximately 39% excess calcium chloride as compared with the standard 53%.

Although there was some improvement in performance five of the thirty-six batches made in this series were weak. The remaining batches varied tinctorially over the usual wide range. Thirteen of the batches were dark and blue, ten were dark and yellow, four were light and blue, and four light and yellow.

It was during the course of the work on this formula that the results were obtained which indicated that the K-1522 type dye (now coded SF-4, K-1971 for plant scale production) tended to give darker, yellower products than the K-1021 dye. Subsequent experience with the K-1522 dye, however, shows only a fair dark, yellow toner production performance which may not be much better than that obtained with the K-1021.

6. Modified K-1436: Batch Size: .05-.1 mol.
Sodium rosinate: Std.
Calcium chloride: 5-10% decrease
Development temp.: 140-155°F.

Attempts to increase the production of yellow tint material by cutting the rosinate used back to the standard K-1436 amount were unsuccessful. Of thirty-six batches made eleven were dark and yellow, four were light and yellow and seventeen were dark and blue. The remaining four batches were of the abnormal weak type.

These products are typical of those being obtained in the Semi-Works with the standard rosinate amount or with slight increases in the rosinate (see results under formula type "5").

Because of the apparently inherent inconsistency of the toner formula it is difficult to draw conclusions as to the effect of the variables used in this Semi-Works production. However, fairly definite effects were obtained with the following variables:

1. Increasing the rosinate up to 35% above the K-1436 amount gave darker masstones and weaker tints (about equal to standard). The K-1436 rosinate amount gave products about 5% strong versus the HT-488-D standard on the average. Tints fluctuate too widely to permit conclusions to be drawn.

2. Development temperatures in the range of 140° to 155°F. usually give dark masstone products of satisfactory strength versus standard. Increasing the development temperature to 165°-175°F. gives lighter masstones and probably very slightly weaker and bluer tints. The use of boiling development in one case gave a very light, weak and blue product versus standard.

3. The quality of the dye used is of principal importance. Most of the K-1021 type dye, especially Semi-Works manufacture, has been giving toners of satisfactory depth and strength. One plant batch of dye made with PTOSA accessory and allowed to stand in pulp form gave very dark, very blue toners at the start but gradully deteriorated to give very weak products.

   Dye manufacture of the K-1522 type (equivalent to the present standard dye formula, K-1971) at first appeared to give darker and yellower material than K-1021 type but subsequent results have indicated an undesirable tendency to give "off" dye which results in very weak toners. Two of the six batches of dye made in the plant using the K-1971 formula have been of this type. Because of the poor quality of the available 2YLM dye it has been necessary to use 2YL dye (supplied by the Dye Works) in toner production. The principal objections to the use of the 2YL type material is the tendency to go light in masstone when batch sizes over .25 mol. are used. Bringing the masstones back into line with rosin increases results in weak tints in the larger batch sizes.

The remaining thirteen Semi-Works batches are considered separately and are divided into the following groups:

1. Three batches were made on the K-1523 toner formula received from the laboratory at the same time as the new dyestuff formula, K-1522. The principal differences between this and the standard K-1436 formula are increased development temperature (156°F. instead of 145°F.) and a 55% increase in the sodium rosinate. Two batches were dark, slightly weak, and yellow as expected, the third batch was "off" (very light and weak).

2. Attempts to rewash some weak toners that showed a bad water bleed by reslurrying with water, striking with an excess of calcium chloride, and then filtering and washing bleed free was successful.

The water bleed was cut from worse to only very slightly worse than standard.

3. Three batches made with a special non-precipitating rosinate have been previously reported in KN-44-20.

4. Six batches of a "straight through" type RT-488-D based on a laboratory formula 974-6B were made with the object of obtaining very dark, very yellow, shading material. These batches were of considerable value as shading material although they showed the following undesirable characteristics.

   a. Dullness of masstone.
   b. Weakness of tint (about 30% weak when shaded to standard tint with blue tint material RT-488-D).
   c. Slightly increased water bleed over normal production.

Most of the undesirable depth of masstone and weakness of tint obtained in this special production may be explained by the fact that the 974-6B formula contains 220#/mol. of rosin as compared with the 140#/mol. figure used in K-1436.

Yields on the Semi-Works RT-488-D production varied over a wide range and averaged only 93% of the K-1436 estimate. Most of the trouble with yields was apparently tied up with considerable pressing losses on the abnormal batches (high water bleed type) together with variation in dye content of the dry color (used "as is"). Normal batches made using the dye on an analyzed basis gave yields almost equal to the estimate.

RT-488-D Toner - Plant Production

Plant production during this period consisted of forty-five batches. Variable combinations based on K-1436 similar to those used in the Semi-Works were tried in attempts to obta in satisfactory quality. Results follow:

1.	Modified K-1436:	Batch Size:	.345-.58 mol.
		Sodium rosinate:	Standard
		Calcium chloride:	"
		Development temp.:	145°-160°F.

Of seven batches made on a formula of this type (practically equivalent to standard K-1436) two were dark and yellow, two were light and yellow, one was dark and blue and one light and blue versus the RT-488-D standard. Strengths on these batches were satisfactory. The remaining batch, made from an abnormal dye lot (92772) was very weak in tint. This is better performance (from the standpoint of obtaining yellow tint) than was secured with a similar formula in the Semi-Works where nearly 50% of the production was on the blue side of standard.

2. Modified K-1436:

Batch Size:	.58 mol.
Sodium rosinate:	Standard
Calcium chloride:	Standard
Development temp.:	170°F.

One batch made on this formula gave a product very close to standard. The batch was judged satisfactory for ink.

3. Modified K-1436:

Batch Size:	.58 mol.
Sodium rosinate:	12 1/2% increase
Calcium chloride:	Standard
Development temp.:	boil

One batch made on this formula ground out very light, 20% weak and very slightly blue versus standard. This result is normal fwr a high rosin, boiling development formula.

4. Modified K-1436:

Batch Size:	.345-.58 mols.
Sodium rosinate:	5-25% cut
Calcium chloride:	5-10% decrease
Development temp.:	170-190°F.

All five batches made on the above formula were of the desired light, yellow type. Tinting strength averaged 5-10% stronger than standard.

5. Modified K-1436:

Batch Size:	.345-.58 mols.
Sodium rosinate:	10-25% cut
Calcium chloride:	5-10% decrease
Development temp.:	145°-160°F.

Fourteen batches were made using this formula. Of these five were dark and blue, two light and blue, one dark and yellow and two light and yellow. These normal batches averaged 10% stronger than standard. The remaining four batches were abnormally weak in tint. Two of the weak batches were made with dye of poor quality (lots 1003 and 1004); no reason can be given for the unsatisfactory strength of the other two weak batches.

6. Modified K-1436:

Batch Size:	.58 mols.
Sodium rosinate:	10-25% increase
Calcium chloride:	Standard
Development temp.:	170°F.

Of two batches made on this formula one was light and blue versus standard RT-488-D. The remaining batch was very weak in tint due to the poor quality of the dye used (lot 92772). No definite quality trend was established in the case of Semi-Works production with a similar formula.

7. Modified K-1436: Batch Size: .345 mols.
Sodium rosinate: std. to 5% increase
Calcium chloride: 5-15% decrease
Development temp.: 145-160°F.

Four dark, blue batches and one light, blue batch were obtained with this formula. Tinting strength averaged 5% stronger than sta ndard. A comparison of these results with those secured with a similar formula except for the use of the standard amount of precipitant (see results under plant toner production formula type 1) would indicate that the precipitant decrease gives bluer tints. However, the dye lots used in these two series of batches were all different and it is probable that the change in dye had a greater effect on hue of tint than the precipitant variation.

8. Modified K-1436: Batch Size: .345-.58 mols.
Sodium rosinate: 10-30% increase
Calcium chloride: 5-15% cut
Development temp.: 145-160°F.

Of six batches made on this formula three were light and blue and three dark and blue. Here again dye quality had a definite effect on the toner. The toner did not respond as well as might be expected to the use of the increased rosinate variable for securing dark masstones.

Remarks concerning the effect of the variables in the Semi-Works production also apply here.

Yields on plant production averaged 95% of the estimate. This is an improvement over the Semi-Works figure of 93% but RT-488-D yield performance may still be considered as poor. It is probable that the use of the dye on an analyzed basis will help to correct this situation.

RM-473-D Production

All of the RM-473-D processed during this period was Muench-mixed. Most of the production was fairly close to standard and was shipped, mixes which finished up on the weak side of the standard were shaded to standard by re-processing with more RT-488-D toner.

Because of the fact that a considerable amount of weak substandard RT-488-D was consumed in this RM-473-D production, the average toner content of these shipments was 49.9% as compared with the standard RM-473-D toner content of 45%. This, of course, added appreciably to the cost of producing RM-473-D during this period.

EXPERIMENTAL DETAILS:

DSN-44-3 Parts I and II Semi-Works Production RT-488-D
DSN-44-14 Semi-Works & Plant Production, Scarlet 2YLN dye, SF-4
DSN-44-15 Plant Production, RT-488-D and RM-473-D.